

Volume V

SCIENTIFIC PAPERS OF C V RAMAN

PHYSICS OF CRYSTALS

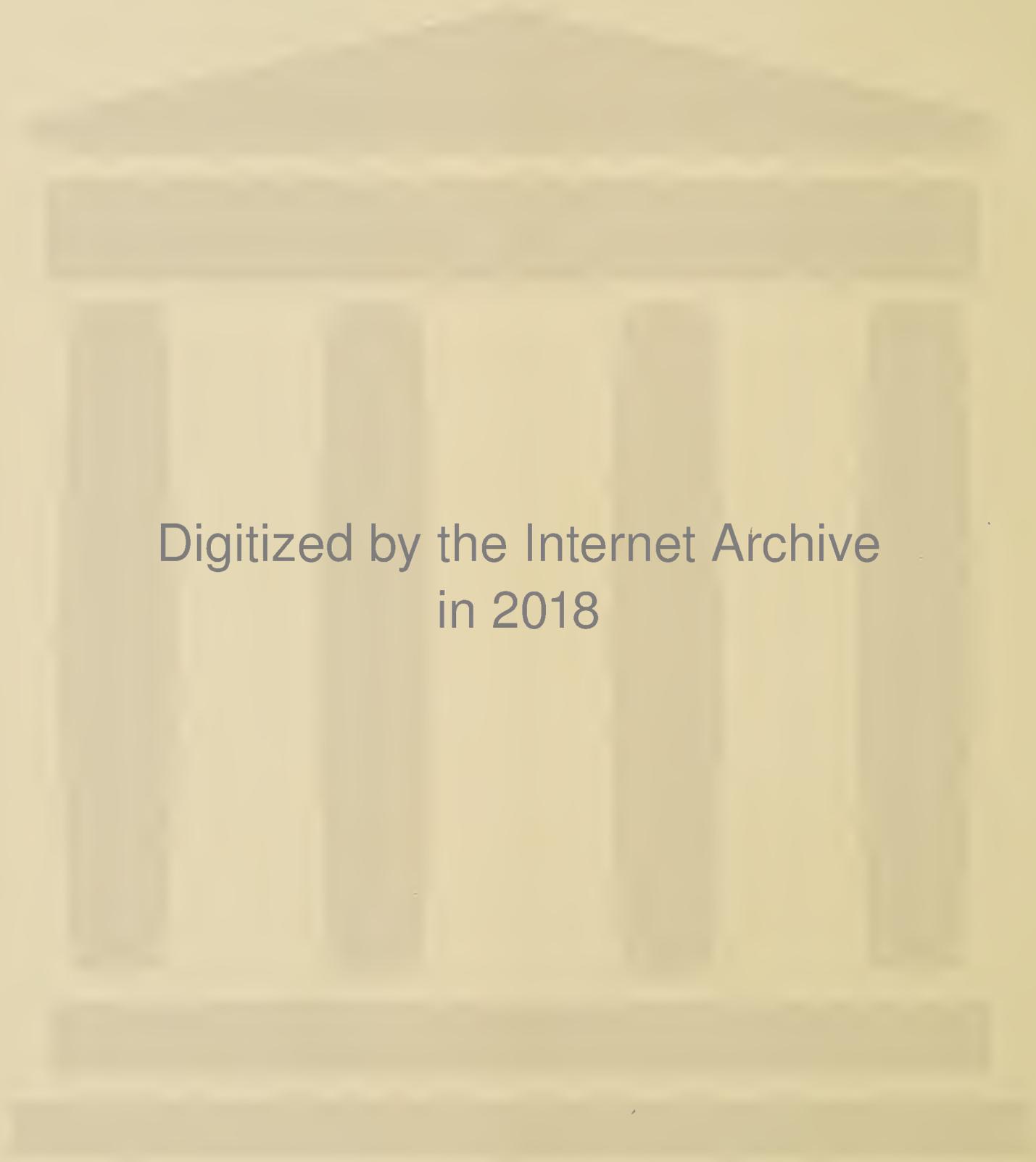


Volume V of the Scientific Papers of C. V. Raman contains the papers published by Raman on various aspects of crystal dynamics. The first set of papers relate to the experimental discovery by Raman and his collaborators of the thermal diffuse X-ray reflections as also the temperature-independent diffuse reflections which Raman thought were due to the interactions of X-rays with optical phonons. There was much dispute about this interpretation of his experiments.

The next set of papers are on the theory of the dynamics of crystal lattices which was also the subject of a raging controversy. It must be said in this context that it was because of the persistent attack by the Raman School that Born's well-known lattice dynamics was re-examined. New physics came out and the concept of singularities emerged clearly. These studies finally showed that Raman's simple theory was a part of the more comprehensive Born theory.

The volume also contains a new view of the theory of elasticity developed by Raman and Viswanathan in which the symmetries of the stress and strain tensors and the number of independent elastic constants differed from the standard view. These papers also proved controversial.





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Scientific Papers of

C V RAMAN

Volume V

PHYSICS OF CRYSTALS



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Edited by

S Ramaseshan



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S RAMASESHAN

INTRODUCTION

Background

Volume V of the *Scientific Papers* represents the work done by C V Raman mainly on various aspects of crystal dynamics. The first set of papers relate to the experimental discovery of thermal diffuse X-ray reflections as also temperature independent diffuse reflections. Raman thought the latter were due to the interaction of X-rays with optical phonons and there was much dispute about this interpretation. The next set of papers are on his theory of the dynamics of crystal lattices which was also the subject of a raging controversy. He then published a large number of papers using his crystal dynamics to calculate the vibrational spectra and the specific heats of crystals. These papers are also included in this volume, as also the four papers in which he and K S Viswanathan developed a generalised theory of elasticity.

Raman's quest for the interaction between optical phonons and matter ended in 1928 but by then he was already looking further. In the lecture *A New Radiation* (1928) he said "If a quantum of radiation can be absorbed in part and scattered in part in the optical region of the spectrum, should not a similar phenomenon occur in X-ray scattering? The type of scattering discovered by Professor Compton may possibly be one of the numerous types of scattering with modified frequencies; some with a line spectrum and some in the nature of continuous radiation."

His foresight was borne out a decade later when he investigated the interaction of X-rays with crystal vibrations. It was known that the possible vibrations in a crystal fall into two broad types. The acoustic spectrum was made up of elastic waves which traverse the crystal in all directions ranging in frequency from zero to a certain upper limiting value as postulated in Debye's very successful theory of specific heats at low temperatures. The second type consisted of "optical" vibrations of the crystal which could also give rise to well-defined spectral lines in infra-red absorption or in the Raman Effect.

Diffuse X-ray reflections

The effect of thermal vibrations on the intensity of X-ray reflections had been considered by many scientists as it was of immediate significance in the determination of crystal structures by X-ray methods. When X-rays fall on an

atom occupying a fixed position in a crystal it would emit in all directions secondary radiations having the same frequency as the primary X-rays falling upon it. In a crystal these secondary radiations cancel in most directions except specific discrete cases in which they reinforce to give sharp (Laue–Bragg) “reflections”. An oscillation of the atom about its position of equilibrium would result in a periodic variation of the phase of the secondary radiation and according to Max von Laue’s analysis in 1926 the secondary radiation itself would have components with frequencies increased and diminished respectively by the oscillation frequency of the atom. As pointed out by Debye and Waller the effect of these vibrations is to decrease the intensity of the X-ray reflections.

Raman pictured these vibrations as periodic pulsations of the electron density equivalent to superposing a dynamic stratification on each static stratification. The phase of oscillation of the atoms varies from one unit cell to the next. A progressive change in the phase of the atomic pulsation in a direction parallel to the particular set of planes is then equivalent to a tilt of the wave-front of the dynamic pulsations away from the static crystal planes. The Bragg condition for the particular spacing (of the periodic pulsation) must be satisfied so that one can get a reflection from the tilted dynamic sets of planes. One notices that this new type of reflection is in a direction which is displaced from the usual geometric position.

Raman had thus shown that X-ray reflections from the static and dynamic planes are separable by the simple device of tilting the crystal away from the correct glancing angle for the X-ray wavelength employed, (a procedure now called exploring the reciprocal space). There should therefore be a measurable intensity of X-rays diffracted in a direction other than the Bragg maximum.

Raman and Nilakantan looked for the existence of such dynamic reflections and observed them in various crystals. In diamond they observed two types of diffuse reflections – one temperature-dependent and the other temperature-independent. These “reflections” from the dynamical periodicity induced by thermal and other waves in the crystal structure are by their nature diffuse i.e. less sharp than the conventional Bragg reflections. The discovery of the non-Bragg reflection probably made for the first time in Raman’s laboratory in 1939 was confirmed by the work of several other laboratories.

Raman derived the correct formulae for the directions of these non-lattice reflections. In working out the theory of the dynamical reflections, Raman emphasized the change of frequency occurring when X-rays interact with the thermal waves, stating that if the X-ray reflections could be analysed by a spectroscope of sufficiently high resolving power, one would find components with the frequency greater and less than that of the X-rays by an amount equal to the frequency of the waves in the crystal. At that time, the diffraction of neutrons had not yet been demonstrated and he was probably one of the few to emphasize the change of frequency and the change of direction of scattering. In fact, it is just the combination of these two measurements that gave the diffraction of slow

neutrons by lattice vibrations and other excitations the fundamental role it now enjoys in exploring condensed matter. Raman's formula showed that in the case of acoustical waves regular geometric reflections would clearly be visible only for small tilts away from the Bragg angle. However the temperature-independent reflections from diamond were sharper and were persistent over much larger angles. Raman and Nilakantan attributed them to the excitation of optical vibrations of the crystal lattice by the X-ray photon and termed the phenomenon "quantum reflection". Strangely enough, Raman was well aware that impurities in crystals under certain circumstances can also give rise to such reflections. Unfortunately, he had intuitively ruled out the possibility of any impurities in diamond. Because of this he was drawn into a long controversy with the distinguished crystallographer Kathleen Lonsdale about these diffuse reflections from diamond which she believed were due to imperfections of various kinds. Years later it was established without doubt that nitrogen and other atoms are present in diamond as substitutional impurities. The extra diffuse spots that Raman and Nilakantan observed were in fact associated with platelets of nitrogen impurities!

It is strange that the discovery of the Raman Effect was due to his intuitive belief that the weak fluorescence which his group observed in light scattering was not due to impurities. But the same intuition seems to have played him false in the case of diamond when he was older by twenty years.

Interest in crystal dynamics

In 1939, using the Raman Effect, Raman and Nedungadi discovered what is now called the "soft mode process" for crystal transformations. In the same year he and Nilakantan also discovered two types of diffuse scattering, one of which he thought was due to the excitation of an optical phonon. These two discoveries made him look for better experimental methods of determining the vibrational spectra of crystals. He was also interested in formulating methods of enumerating these vibrations and computing their frequencies, at least in the case of simple crystal structures like rock-salt, diamond, etc. It was at this stage that he returned to the remarkable photograph of the Raman spectrum of NaCl published by Fermi and Rasetti in 1931. They illuminated a 5 cm-thick NaCl crystal with the 2536.5 Å resonant radiation from a magnet-controlled water-cooled quartz mercury arc. To prevent the complete fogging of the photographic plate which would have resulted from long exposures with intense illumination, Rasetti had introduced a filter of mercury vapour which absorbed the resonance radiation producing a clear photograph in which the spectral lines could have been seen as close as fifty wavenumbers from the incident line. The actual spectrum recorded was the second order Raman spectrum of NaCl (the first order being forbidden by symmetry). It was described by them as follows: "The effect is however very

different from the usual Raman effect observed in crystals. It consists of a continuous spectrum over which were superposed a few apparently randomly distributed maxima and minima." Raman discerned in these "randomly distributed maxima and minima" nine "lines" which was exactly the number of vibrations of the NaCl lattice expected on the basis of his theory.

So impressed was Raman with the Rasetti technique that he urged his associates to set up this arrangement immediately in his laboratory and if possible improve upon it by using higher dispersion spectrographs. The second order Raman spectra of NaCl and diamond were recorded by R S Krishnan and in his skilful hands it became perhaps the best method for studying the vibration spectra of crystals till it was overshadowed by the use of lasers.

Reformulation of crystal dynamics and its achievements

Raman formulated his crystal dynamics starting from the classic work of Lord Rayleigh. In a normal mode of a connected system of particles, they all vibrate with the same frequency and can have either the same or opposite phases. Raman then introduced the basic principle of crystal architecture: that the crystal consists of sets of equivalent atoms ordered in such a manner that each atom in a set is both geometrically and physically related to its environment in exactly the same way as every other atom of the same set. He deduced that in a normal mode of a crystal, equivalent atoms in it, all have the same amplitude of vibrations, their phases being either the same or else opposite in successive cells of the lattice along each of the three axes. This is equivalent to saying that atomic vibrations repeat themselves exactly in a space pattern of which the unit has twice the dimensions in each direction and therefore eight times the volume of a unit cell of the crystal lattice. If, therefore, each unit cell contains p atoms then these cells contain $8p$ atoms and these have $24p$ modes of vibration or $(24p - 3)$ normal modes if one excludes the three translations. Hence according to Raman the fundamental result emerges that a crystal containing p interpenetrating (Bravais) lattices of atoms has only $(24p - 3)$ characteristic modes of vibration each of which is characterized by a specific frequency. In $3p - 3$ of these modes equivalent atoms have the same phases of oscillation in adjacent cells and in the $21p$ other modes the amplitudes are the same, while the phases alternate in adjacent cells (along one, two or three axes of the lattice).

Raman next proceeded to give a physical picture of the $21p$ modes in cubic crystals. For example, in the case of rock-salt these modes are oscillations of the alternate planes of equivalent atoms in a crystal relative to each other, the planes being either the octahedral planes or the cubic planes. The degeneracies were then calculated and the modes enumerated to be nine for NaCl, eleven for CsCl, and eight for diamond etc. The description of each mode was given. The numbers in

almost every case corresponded to the numbers of the peaks observed in the second order Raman spectra of these crystals. He then proceeded to calculate the frequencies of these $24p - 3$ modes for many crystals in terms of force constants. The agreement between calculated frequencies and the experimentally observed ones was very good. He then calculated the specific heats of these crystals assuming the frequency spectrum to consist of $24p - 3$ discrete frequencies and using them as simple Einstein oscillators, with an appropriate Debye term added. Again the agreement between theory and experiment was rather good.

The large number of papers on the Raman spectra and infrared spectra of a number of crystals had valuable experimental data and good fits with theory and one would have thought that all these indicated a success of his ideas. Indeed, if these papers had been presented as a simple and physical approximation capturing the essential features of optical modes, they would have been regarded as a significant contribution in the field. But to Raman, the successes of his approach meant that the entire body of lattice dynamics as formulated by Born and von Karman and developed by Born and his students was completely wrong. He launched a scathing criticism of their ideas on fundamental grounds. This period was marked by bitter controversy, basic errors, and much wasted time and effort on his part, and can only be described as a tragic failure.

The lattice dynamics controversy

Raman deduced that a crystal having N cells (with p particles in each cell) has only $(24p - 3)$ modes. His critics pointed out that this is in direct conflict with Lagrange's theorem which states that a dynamical system composed of Np particles has $3Np - 3$ normal modes. Since N is large for real crystals, theory predicts that the phonon spectrum must be continuous, in conflict with Raman's assertion that it is discrete; and further $(24p - 3)$ is a very small number compared to the actual number of degrees of freedom of a crystal. Of course, it should be mentioned that in fitting the specific heats of solids, Raman used the correct total number of degrees of freedom, which means that he regarded his modes as highly degenerate.

Raman's perceptive student K S Viswanathan, starting from the conventional lattice dynamics, proved that the group velocities of the lattice waves vanish for these special modes, which correspond to the limiting (zone centre or zone boundary) optical modes. Since the density of states in the frequency spectrum is inversely proportional to the group velocity of the waves, these (Raman) modes correspond to singularities which are particular cases of those classified in general by van Hove a few years later. From the conventional lattice dynamics it can be shown that these frequencies should appear as maxima in the Raman spectra of crystals and in this way the theory is consistent with Raman's observations. It was pointed out correctly that even if the group velocity vanishes for this handful of

($24p - 3$) modes, it does not mean that the other modes do not exist, nor does it mean that the frequency spectrum is discrete.

Raman rejected the notion used by Born and von Karman that normal modes could be described in terms of travelling waves. To him the Born cyclic postulate was an artificial device without any physical meaning. This particular criticism of Raman seemed a valid one and therefore many theoretical physicists looked into it. For example, Peierls proved that the normal modes in a crystal with boundaries are by no means identical to those of a cyclic crystal (with no boundaries) but the frequency spectra of the two are practically identical if the ratio of the number of atoms on the surface to those in the bulk is small. Thus except in special situations where surface effects are likely to be important the mathematically simpler (though artificial) picture given by the cyclic postulate is a very good approximation. It is of some interest that Peierls published this paper in an Indian journal.

Since Raman started from the correct definition of the normal mode given by Rayleigh, at what stage did the theory take a wrong turn? It is in his second assertion that in a normal mode in a crystal, equivalent atoms in adjacent cells must vibrate with the same amplitude with the same or opposite phases. This is reminiscent of the famous Bloch condition in solid state physics which is only valid for travelling waves! Raman inappropriately imposed this condition on a standing wave situation which completely restricted his attention to 8 cells. Although this proved important in explaining and calculating the frequencies at the "zone centres" and "zone boundaries" and explained some important features observed in the second order Raman spectra of crystals, the nature of the complete lattice spectrum was missed.

This volume also contains papers on a new view of the theory of elasticity in which the symmetries of the stress and strain tensors and the number of independent elastic constants differed from the standard view. These papers naturally proved controversial as well.

The controversies in perspective

This volume contains many papers based on ideas which were hotly disputed even in Raman's time and are recognized to be incorrect today. It is probably natural that a scientist who relies on his powerful intuition (as Raman did) would sometimes be led into errors. The experimental proof of the spin of the photon has already been mentioned in Volume I and the intrinsic tetrahedral symmetry of diamond in Volume IV. In this volume, we have his view that the excitation of optical phonons was the cause of the temperature-independent diffuse X-ray reflection in diamond. In all these cases, it is fair to say that the state of knowledge at that time left genuine room for doubt. It is true that in his later years, Raman was prone to ignore or dismiss evidence which contradicted his point of view.

His work on the foundations of lattice dynamics stands apart from the three instances given so far. Firstly, it concerned a subject in which he was an acknowledged master – waves and vibrations. One sees a combination of many factors which shaped his strong, unyielding and ultimately incorrect objections to Born's theory of lattice dynamics. To start with, the artificial looking cyclic postulate must have put Raman off. Elaborate calculations (not fully carried out till the advent of computers a decade or more later) were needed to predict the simplest of optical and thermal properties from the Born theory. Lacking the notion of singularities in the spectrum, again not to come for a decade, the sharp features seen in the Raman scattering found no explanation. In this situation it is natural that Raman sought an alternative, and once it turned out to match the experiments, he was blind to its theoretical flaws. By the time the crucial evidence in favour of the Born theory had accumulated, his attitude had hardened and even his close associates and students could not get through to him on this subject. More than any of the other errors mentioned earlier, it was his stand on lattice dynamics which genuinely diminished his stature as a scientist in later years. While this controversy (and others to a lesser extent) caused a great deal of pain to those around him at that time, they fit into a pattern which is not at all unusual in the history of science. The same qualities (intuition and persistence in Raman's case) which are responsible for a scientist's great successes can also let him down on other occasions. It is essential for the biographer, historian or even the student of science to be well aware of this side of Raman and hence these papers have been reprinted here in full to give a complete picture of the man. But in the long run, there is no doubt that Raman's towering contributions to so many areas of physics – exemplified by the other volumes of his collected papers – will outweigh by far the errors of interpretation and judgement we have just discussed.

*RAJARAM NITYANANDA
S RAMASESHAN*

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THE PAPERS

A new X-ray effect

SIR C V RAMAN
and
DR P NILAKANTAN

The discovery by Laue in 1912 of the diffraction of X-rays by crystals and the discovery by A H Compton in 1922 of the change of wavelength in X-ray scattering had both a profound influence on our concepts of the nature of X-radiation. Laue's discovery established beyond all question that X-rays are physically of the same nature as ordinary light but of much shorter wavelength, while the Compton effect showed in the clearest possible way that the interaction between X-rays and matter obeys quantum mechanical principles. The new X-ray phenomenon described and illustrated in the present communication has, in its physical nature, something in common with both the Laue and the Compton effects: it is a specular reflection of X-rays by crystals but with a change of frequency explicable only on quantum mechanical principles. Before proceeding to give particulars of the phenomenon, it would appear desirable to make a few prefatory remarks regarding the structure of crystals and the nature of their internal vibrations:

The ideal crystal is an ordered geometric arrangement of atoms or molecules held together in a space-lattice by interatomic forces. The electron density in such a crystal is a periodic function in space expressible as a three-dimensional Fourier series. Each term in this Fourier expansion contains as a multiplying factor the structure-amplitude which is the magnitude of the periodic variations of electron-density occurring as we proceed along the particular direction in the crystal. This same factor determines the amplitude and phase of X-rays reflected by the particular spacing in the crystal in the conditions indicated by the Bragg formula.

The internal vibrations possible in a crystal are of two types. The first type is the acoustic spectrum of elastic waves which traverse the crystal in all directions and range in frequency from zero up to a certain limiting value; these figure in the Debye expression for the specific heat of the solid. The second type consists of the characteristic vibrations of the crystal giving rise to well-defined spectral lines in infra-red absorption or in the scattering of monochromatic light; these appear as Einstein functions in the expression for the specific heat. We are here particularly concerned with the nature of the internal disturbances in the crystal corresponding to the Einstein functions. It would be wrong to identify them with incoherent

vibrations of the individual atoms or molecules in the lattice. Indeed, in a perfect crystal, the correct way to picture them would be to regard them as a vibration of the inter-penetrating lattices forming the crystal as rigid wholes relatively to each other, so that the phase of such vibration is the same everywhere throughout the crystal.

Since the structure-amplitude corresponding to any particular spacing in the crystal depends on the positions of the atoms in the unit cell of the lattice, it is clear that a periodic vibration of the inter-penetrating lattices would cause a corresponding variation with time of each structure-amplitude. If, therefore, the crystal is traversed by a beam of monochromatic X-rays, the Bragg reflections (where these are possible) would also be affected by the periodic variation of structure-amplitude. Viewed in a classical way, this would mean that the intensity of the Bragg reflection, instead of being constant with time, would be modulated by the infra-red frequency. In other words, if the X-ray reflections could be analysed by a spectroscope of sufficiently high resolving power, we would find three components, one having the original frequency of the incident monochromatic X-radiation, and the other two, a frequency greater and less respectively than this frequency by that of the internal vibration in the crystal.

The foregoing classical view-point, though it serves to indicate the possibility of X-ray reflections with altered frequency, is fundamentally inadequate. As in the case of the scattering of light with change of frequency, it fails to tell us exactly what we do observe. For instance, in the classical theory, reflections with relatively large changes of frequency could not occur, as the corresponding lattice vibrations would not be thermally excited to any appreciable extent. On the principles of the quantum theory, however, the position would be different; the lattice-vibration, even when of high frequency and therefore not initially present, would be excited by the incidence of the X-ray itself. The intensity of the reflection with change of frequency would in fact depend on the change of structure-amplitude as indicated by the classical considerations, but the law of temperature variation would be altogether different.

The quantum view-point also indicates that we may expect to be able to observe the modified reflections independently of the unmodified ones, instead of merely accompanying them as is indicated by the classical considerations. To appreciate why this is the case, we have only to recall that the reflection of the usual type cannot occur if the spacing in the crystal, the angle of incidence and the wavelength of the incident monochromatic X-rays do not satisfy the Bragg formula. The modified X-ray reflections are, however, not determined by the fixed positions of the atoms in the crystal, but by their displacements from the same. By a suitable adjustment of the phases of these displacements, the planes of constant phase may be inclined at an angle to the crystal spacings in such manner as to satisfy the Bragg relation for the modified reflections. In other words, we would get a modified reflection from a given set of crystal planes even when an unmodified one is not possible with the given X-ray wavelength.

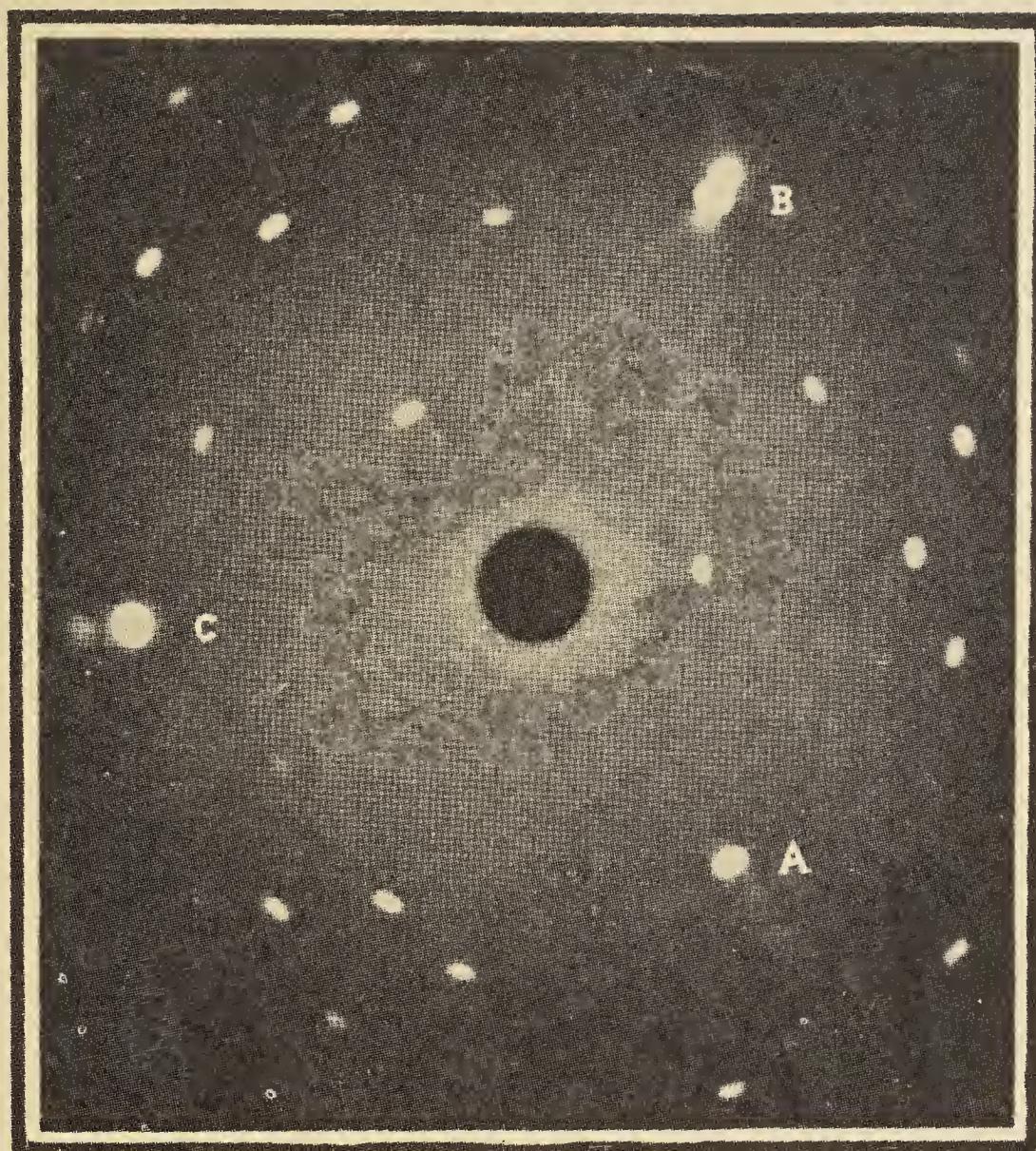


Figure 1. Laue pattern of diamond showing the new effect.

Modified X-ray reflections of the kind discussed above are to be seen in figure 1 which is a Laue photograph obtained with a crystal of diamond, the X-rays being from a tube with copper target excited at 41,000 volts. The crystal plate which had its faces parallel to one of the octahedral cleavages of diamond was so set that the incident X-ray beam was nearly normal to the crystal faces. The white radiation present gives the usual Laue spots, the pattern exhibiting approximate trigonal symmetry. The three most intense spots in the pattern (marked A, B, C in the figure) are the reflections from the $[111]$ planes parallel to the three other octahedral cleavages of the diamond. It will be noticed that these spots are accompanied by companions which lie on the radial lines joining them with the centre of the pattern, the positions and intensities of the companions being however different. Spot A has two faint companions lying outside. Spot B has also two companions lying one on either side of it, while spot C coincides with the inner one of its own companions. These companions are the modified reflections of the $\text{Cu } K_{\alpha}$ and $\text{Cu } K_{\beta}$ radiations, and the spacing of the planes responsible for them is the same as that of the $[111]$ planes in the crystal, though of course, their inclination to the incident beam is different, as explained above. The striking

variation in the intensity of the spots is evident in the picture and is clearly related to their position relatively to the [111] Laue reflections. In fact, the intensity of the modified reflection is seen to fall off rapidly with the increasing inclination of the phase-waves to the [111] spacings.

The case of the diamond is of exceptional interest, both because of the fact that it approaches closely to an ideal crystal, and also because of the simplicity of its crystal structure which consists of two similar interpenetrating lattices. The frequency of the vibration of these two lattices relatively to each other is known from studies on light-scattering in diamond to have the high value of 1332 cm^{-1} in spectroscopic units or in absolute measure, 40×10^{12} per second. It will be seen on examining a crystal model of diamond that an oscillation of the two lattices relatively to each other would cause a large variation of the structure-amplitude of the crystal for the [111] spacings. The frequency of the vibration is so high that at the ordinary temperature its thermal excitation is negligible. The fact that the modified reflections are as intense as they are is thus explicable only on the quantum point of view.

In addition to the modified reflections, figure 1 shows other features of great interest, e.g., a diffuse halo falling off in intensity as the [111] reflections are approached and faint streamers stretching out obliquely from the modified reflections. Into the explanation of these features, we shall not here enter.

Reflection of X-rays with change of frequency— Part I. Theoretical discussion

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1. Introduction

The present paper deals with the new type of X-ray reflection in crystals observed by the authors and described in an address to the Easter Conference of Scientific Societies at Bangalore on the 22nd March of this year. A brief account of the phenomenon with an illustrative photograph of the effect as observed in diamond appeared as a special article¹ in the issue of *Current Science* for April under the title “A new X-ray effect”. The phenomenon was there described as having “in its physical nature, something in common with both the Laue and the Compton effects”, and as being “a specular reflection of X-rays by crystals but with a change of frequency explicable only on quantum mechanical principles”. More succinctly, we may describe it as the analogue in X-ray optics of the phenomenon of the scattering of light in crystals accompanied by a change of frequency. The appropriateness of these descriptions will be made evident as we proceed.

Twenty-two photographs grouped in eight plates accompany Parts II and III of the present paper (appearing in the same issue) and are intended to illustrate various aspects of the new phenomenon. Detailed studies have been made with two crystals, namely, diamond and sodium nitrate, which fully establish the nature of the effect and confirm the theoretical interpretations which have been put forward. These are also set out with full particulars.

2. Scattering of light in crystals

In the lecture² on “A New Radiation” (Raman 1928) describing the phenomenon of a change of frequency in the scattering of light by matter, the issue was raised whether such scattering should be considered as being coherent or non-coherent radiation, in other words, whether the different molecules in the substance emit

the scattered radiation with or without any definite phase-relationships as between themselves. It was suggested that though the assumption of incoherence might seem a natural one to make, nevertheless the question required investigation before a definite answer could be returned. Considering the purely theoretical issue, it is evident that if the molecules in a substance are independent oscillators, the scattered radiations arising from the transfer of energy to them need obviously have no specifiable phase-relationships. The position would however be different when the molecules are packed and held together as an ordered assemblage in a crystalline solid by interatomic forces. In such a case, the oscillations with which we are concerned would be those of the crystal lattice rather than those of the individual atoms or molecules. The transfer of energy from the radiation to the substance should then evidently be regarded as a process in which the crystal as a whole is the operative unit. This point of view was indeed suggested and adopted³ by Ig Tamm (1930) as the basis for a quantum-theoretical discussion of light-scattering in crystals.

The simplest mechanism by which a change of frequency can be produced in light by the co-operative action of the molecules in a substance is that considered many years ago by Leon Brillouin⁴ in a well known paper (1922). Addressing himself to the problem of the diffusion of light by the thermodynamic fluctuations of density in a substance, Brillouin considered the effect on a beam of light of a plane train of sound-waves traversing the medium. The sound-waves result in a periodic stratification of the optical density of the medium, and hence in accordance with a well known optical principle would selectively reflect the light-waves, provided these are incident on the stratifications at a glancing angle θ satisfying the relation

$$2\lambda^* \sin \theta = \lambda \quad (1)$$

λ and λ^* are the wavelengths of light and sound respectively as measured in the medium. The optical stratifications due to the sound-waves are, however, not static but travel through the medium with the usual acoustic velocity v . Accordingly, there would be a Doppler effect giving a change of frequency in the reflected light. This would be an increase or a decrease according as the sound-waves approach or recede from the light source. The change of frequency is given by the usual formula for reflection from a moving mirror, namely

$$v_{\text{reflected}} - v_{\text{incident}} = \pm 2 \cdot v \cdot \frac{v}{c} \sin \theta \quad (2)$$

c being the velocity of light in the medium. Writing $c = v\lambda$ and $v = v^*\lambda^*$ where v and v^* are the frequencies of the incident light and sound-waves respectively, and combining equations (1) and (2), we have the relation,

$$v_{\text{reflected}} - v_{\text{incident}} = \pm v^*. \quad (3)$$

In other words, the change in the frequency of light in a Brillouin reflection is

merely the frequency of the periodic pulsation in the optical density of the medium.

In the case considered by Brillouin, the sound-waves are those spontaneously existing as the result of the thermal agitation in the substance. The wavelength λ^* of the sound which is actually operative is automatically determined by the wavelength λ of the light and the glancing angle θ as per equation (1). As λ^* diminishes from ∞ to $\lambda/2$, θ varies from 0 to $\pi/2$, and hence the specular reflection by the sound-waves actually gives a scattering in all directions with a change of frequency depending on the direction as indicated by (2). As the velocity of sound is small compared with that of light, this change of frequency is also small. Nevertheless, it has been established experimentally for the case of light-scattering in liquids, and more recently⁵ also in crystals (Raman and Venkateswaran 1938).

It should be remarked, that the optical principles on which equations (1) and (2) rest are of very general validity, and we are not therefore restricted to the cases in which the dynamic stratification in the medium may be identified with ordinary sound-waves. We may, in fact, start from (3), and consider a case in which a pulsation of optical density occurs in the medium with a specified frequency ν^* which may be much higher than that of any sound-waves permissible in the medium. We may assume further that the pulsation, instead of occurring with identical phase throughout the otherwise homogeneous medium, appears as a periodic stratification having a wavelength λ^* and travelling through the medium with a phase-velocity which is not identical with the ordinary acoustic velocity and indeed may be vastly greater. The stratifications would then give rise to a reflection of the incident light-waves with a change of frequency ν^* as in the case already considered, provided that the wavelength of the stratifications and their inclinations to the incident light-waves satisfy the relation (1).

The foregoing discussion indicates that when light is scattered by a homogeneous crystalline solid with a change of frequency ν^* corresponding to one or other of the characteristic infra-red frequencies, the process which occurs may be pictured as follows: The effect of incidence of the light-waves on the crystal is to generate in the latter, periodic stratifications of optical density having the frequency ν^* and a wavelength λ^* , the latter depending on their inclination to the light-waves. These stratifications reflect the light with altered frequency in the manner indicated by equations (1) and (3). The appropriate wavelength of the stratifications and their inclination to the incident light-waves are determined by the act of reflection itself. Surprising as this picture may seem, it is difficult to avoid the acceptance of it, once we concede the idea that the process of light-scattering in a crystal is a coherent phenomenon. Indeed, it is obvious that a completely homogeneous medium can scatter no light even if it is pulsating periodically. The presence of appropriately spaced and inclined stratifications of the pulsation is therefore a necessity to explain the observed scattering.

We may, at this stage, well ask ourselves the question, is there any experimental

evidence to support the basic postulate of coherence? It should be remarked in this connection, that measurements of the intensities of the scattered radiations cannot furnish a direct reply to this question. At first sight, it might seem that 'coherent' scattering should give us a much larger scattering than the 'incoherent' variety, and indeed this would be the case if the strength of the optical dipoles in the scattering particle is prescribed beforehand. Actually, however, when numerous oscillators co-operate in taking up energy from the incident quantum of radiation, their individual dipole strengths are reduced in proportion, and hence, when they emit the quantum again in co-operation, the final result is practically unaffected. The evidence actually available which indicates that light-scattering in crystals is a coherent process is rather indirect. It is well known that the frequency shifts given by crystals often differ appreciably from those obtained in the gaseous or liquid condition of the same substance, and are generally represented by sharply defined lines in the spectrum. Further, the selection rules for the intensity and polarisation of the scattered radiations appear, at least in the cases so far examined, to be determined by the structure and symmetry of the crystal as a whole, rather than by the structure and symmetry of the ionic or molecular units contained in it. These facts are significant and clearly favour the coherence hypothesis. This evidence is however, not absolutely conclusive and we have to rely more on the a priori probabilities of the case. If we consider a crystal such as diamond or quartz consisting of chains of atoms linked together firmly and continuously by valence bonds, it would be difficult to concede that the scattering of light in it could be the result of incoherent local processes involving only individual atoms. Such a crystal as diamond or quartz has been aptly described as being itself a giant molecule, and it appears quite natural to regard the solid as a whole and not the individual atoms in it as the scattering units. Indeed it may be said that nothing so far observed definitely contradicts the postulate of coherence in light-scattering as applied to crystals.

3. Effect of pulsation of structure-amplitude

In his paper of 1922, Brillouin applied his theory of reflection by sound-waves to the problem of the diffusion of X-rays when passing through a crystal which results from the thermal agitation in it. It is clear from equation (1) that such reflections would, as in the case of light, give rise to a diffusion or scattering of the radiation. But owing to the short wavelength of the X-rays, such diffusion would be limited to glancing angles ranging from zero up to a maximum determined by the shortest wavelength of sound present in the acoustic spectrum of the crystal. As this wavelength limit for sound can scarcely be smaller than the grating constant of the crystal, the diffusion of the Brillouin type would be limited to

glancing angles less than that at which any Bragg reflection of monochromatic X-rays by the crystal could appear.

As in the case of light, however, we are not restricted to considering stratifications which are identifiable with sound-waves, and may extend the application of equations (1), (2) and (3) in the X-ray region to any type of coherent pulsation capable of giving periodic stratifications of the electron density of the crystal. Excluding the case of small glancing angles, we see from (1) that the wavelength λ^* of the stratifications must be comparable with that of the incident X-rays, and would therefore also be of the same order of magnitude as the crystal spacings existing in solids which give the ordinary Bragg reflections of unchanged frequency. It is therefore necessary to consider in what circumstances, the dynamic X-ray reflections with change of frequency here contemplated may be expected to occur with sensible intensity and be capable of being distinguished from the usual static reflections.

As is well known, the usual Laue spots given by X-rays with crystals are observed when the Bragg condition given by (1) is satisfied, λ^* now representing the spacings in the crystal structure, and λ the wavelength of the X-rays responsible for the reflection. The intensity of any such reflection is determined principally by a quantity known as the structure-amplitude of the spacing, which appears as a multiplying factor of the corresponding term in the three-dimensional Fourier analysis of the electron density in the crystal. This structure-amplitude is determined by the atomic arrangement in the unit cell of the crystal lattice. If, now, we postulate a periodic pulsation of the atomic positions in all the cells of the crystal lattice, its effect would be to vary the structure-amplitude of every spacing of the crystal periodically with the same frequency. In other words, the effect of such pulsation is to superimpose upon the each static structure-amplitude of the crystal, a dynamic structure-amplitude having the same spacing and capable of giving a reflection with changed frequency.

We may now, in the first instance, consider the consequences of assuming that the phase of the pulsation of electronic density is rigorously the same for all the unit cells in the crystal lattice. The static and dynamic stratifications of electron density would then everywhere run parallel to each other, and the geometric conditions (as given by the Bragg formula) for the appearance of static and dynamic X-ray reflections would therefore be identical. In other words, the unmodified and modified X-ray reflections would always appear or fail to appear, at the same time. Since the actual change of frequency in the X-ray reflections is beyond the resolving power of the most powerful X-ray spectrometer, we should be unable to detect the appearance of the modified reflections in the presence of the unmodified ones.

Actually, however, the assumption that the pulsations in the cells of the crystal lattice are coherent does not imply that their phases should be identical at all points of the crystal. Indeed, we have already seen that in order to explain the phenomena observed with ordinary light, it is necessary that the analogous

pulsations of optical density in the crystal should *not* be of identical phase throughout, but should appear as stratifications having the appropriate wavelength and inclination to the incident light-waves and thus satisfying the condition for a coherent reflection. In our present case, the spacing or wavelength of the dynamic stratifications is fixed, being in fact the atomic spacings in the crystal, but their phases are capable of adjustment and should, in fact, automatically adjust themselves, as in the case of light, so as to secure the condition necessary for reflection. *It is readily seen, that a progressive change of phase in the atomic pulsations as we move in a direction parallel to a particular plane of atoms is equivalent to a tilt of the wave-front of that pulsation away from the crystal planes in a direction perpendicular to them.* When a pencil of X-rays is incident obliquely on a particular spacing of the crystal, the phase of the electrical vibration reaching successive atoms in any particular layer alters progressively in the plane of incidence. A compensating change in the phase of the structure-amplitude variation along the same direction would, in effect, tilt the wave-fronts of the atomic pulsation to such an obliquity that the Bragg condition for the particular spacing may be satisfied. In other words, we can get a dynamic or modified X-ray reflection from a particular atomic spacing at an angle of incidence at which we cannot obtain the usual Bragg reflection for the same X-ray wavelength. The modified reflection would in these circumstances appear in a direction which is displaced from the usual geometric position.

The foregoing discussion indicates that the unmodified and modified X-ray reflections are separable by the simple device of tilting the crystal away from the correct glancing angle for the X-ray wavelength employed. The unmodified reflection obeys the usual geometrical laws of reflection from the atomic spacings besides satisfying the Bragg condition. The modified reflection also appears in the plane of incidence of the X-ray on the atomic spacings, but in general, in a direction different from that of geometric reflection from such planes. This failure of geometrical optics is, however, more apparent than real; as we have already seen, the modified reflections satisfy both the geometrical laws of reflection and the Bragg condition, provided that we recognise the surfaces of constant phase of the structure-amplitude pulsations and not the atomic spacings themselves as the reflecting planes responsible for them.

4. Modified reflection as a quantum effect

It is well recognised that the scattering of light with a change of frequency as actually observed is a quantum effect and cannot be explained on the classical dynamics, though there is a classical analogue which agrees with it in certain particulars. The inadequacy of the classical theory is evident even in the case of scattering by individual molecules and becomes clearest when we consider the question of intensities. Taking, for instance, the scattering of light by a hydrogen

molecule, the characteristic vibration frequency is 4156 cm^{-1} in spectroscopic units. Classically, the spectrum of monochromatic light scattered by hydrogen gas should exhibit two spectral lines of equal intensity shifted from the primary radiation in either direction by this frequency. But the intensity of either of the displaced lines on the classical theory would be very small, while in actual fact, this is true only of the line displaced to a higher frequency, whereas the line shifted to a lower frequency is remarkably intense. When we consider light-scattering in crystals, the failure of the classical theory is even more acute. Classically, a crystal if it is an ideally homogeneous solid, should scatter no light at all; in order to explain the observed diffusion of light, we have to postulate that stratifications having the desired frequencies and of specially suitable wavelengths and orientations are present which reflect the incident radiations with a change of frequency. Except for the lowest frequencies of pulsation or at sufficiently high temperatures, thermal agitation would scarcely be adequate to account for the presence of such stratifications. This difficulty disappears when light scattering is regarded as a quantum-mechanical phenomenon, as the production of the stratifications which reflect the radiations would then itself be a part of the process.

In our present X-ray problem, the stratifications with which we are concerned have, in part, a physical basis, namely, the atomic spacings in the crystal, and this fact is responsible for the resulting effects being directed reflections analogous to the Laue spots instead of being a diffuse scattering. The atomic pulsations which give the periodic variations of structure-amplitude have the same origin as the characteristic internal vibrations revealed in light-scattering or in infra-red absorption, and their frequencies may be so high that the thermal excitation of the same is entirely negligible. Nevertheless, as in the optical case, we should expect them to be excited and give rise to the modified reflection of X-rays even at ordinary temperatures. Further, on the quantum view, such modified reflections should persist without serious diminution of intensity when the crystal is cooled down to low temperatures. *Per contra*, when the crystal is heated, the intensity of the modified reflections should increase but not very greatly until temperatures are reached at which the characteristic vibrations concerned contribute notably to the thermal energy content of the crystal.

As we have already seen, the appearance of the modified reflections in directions other than that of the unmodified ones involves a suitable progression of the phase of the atomic pulsation in the plane of incidence. This "tilting of the wave-fronts" so as to secure the possibility of a Bragg reflection at any arbitrary angle of incidence might seem a very surprising postulate to make when we view the subject classically. But it fits in perfectly with the quantum mechanical point of view according to which the incident radiation itself creates the atomic pulsations which result in its reflection, and the conditions necessary for such reflection are therefore automatically secured. Even on a purely classical view, it is not inevitable that the pulsations in the crystal lattice should be of identical

phase everywhere, though the more rigidly constructed the crystal lattice is, the more closely this ideal might be expected to be approached, and the more sharply would the modified reflections be limited to directions approaching that of the unmodified ones.

5. Analogy with the Compton effect

As is well known, the change of wavelength in X-ray scattering discovered by A H Compton in 1922 was explained by him⁶ as the result of the transfers of energy and momentum which occur when a photon impinges on a free electron. In the wave-mechanical picture of the same process given by Schrodinger⁷ in 1927, the scattering of the photon appears as a reflection of the incident waves by the periodically stratified distribution of charge density obtained on superposing the De Broglie waves of the electron before and after the collision. The Doppler effect due to the movement of these stratifications explains the change of frequency in reflection. That the effect as actually observed is a diffuse scattering follows from the fact that the recoil of a free electron and therefore also the reflection of the incident radiation is in an arbitrary direction. The wave-mechanical picture of the Compton effect is thus rather similar to Brillouin's classical treatment of the reflection of light by travelling sound-waves. The analogy would be closer still if the stratifications of optical density in the medium were considered as resulting from the incidence of the radiation, as in Schrodinger's treatment, instead of being postulated to exist in advance.

That the change of wavelength in the Compton scattering is a function of the angle of observation follows from the manner of its origin. Several attempts have been made in the past to observe the change of wavelength independent of the angle of scattering which might be expected if the electron which scatters the radiation shifts to a higher energy level while remaining bound to the atom. The theoretical problem has been considered⁸ by Sommerfeld in whose note will be found references to various papers in this connection. It is clear that if such an effect exists, the change of wavelength would be much smaller than the Compton shift. Then again, the more firmly the electron is bound to the atom, the less likely it is as the result of the scattering process, to pass to an unoccupied level of higher energy. These circumstances and the necessarily feeble intensity of any effect which appears as a diffuse scattering would militate against its successful detection in experiment. It may be recalled in this connection that the attempts so far made to discover the analogous phenomenon of a change of frequency in light scattering due to the transfer of a bound electron from one energy level to another within an atom have also been unsuccessful.

The preceding discussion prepares us for recognising that the modified reflection of X-rays by crystals and the Compton effect are essentially analogous phenomena, as they both arise from the reflection of radiation by a stratified

distribution of electric charge density. There are however also significant differences. In our present case, the electrons remain bound to the crystal lattice of which they form a part, and the stratifications arise from the crystal lattice being set in vibration and causing a periodic variation of the electronic charge density in the crystal structure. Accordingly, in our present case, the resulting effect appears as a directed reflection instead of as a diffuse scattering. The frequency changes in the modified reflection of X-rays are necessarily much smaller than in the Compton effect, indeed so small as to be beyond spectroscopic detection. The differences between the laws of modified and of unmodified reflection of X-rays by crystals should however enable us to recognise their existence.

The analogy between the modified reflection of X-rays and the Compton effect will also be obvious when it is recalled that in the present case as well, the change of frequency and the change in direction of the reflected X-rays may be regarded as a consequence of the exchange of energy and momentum between the incident quantum of radiation and the crystal lattice. The discussion of this point may however be more suitably undertaken in a later paper in which the intensity problem for modified X-ray reflection will be more fully dealt with.

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Reflection of X-rays with change of frequency— Part II. The case of diamond

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1. Introduction

We may now proceed to describe the results obtained by using the Laue method with various crystals which demonstrate the phenomenon of modified X-ray reflection and indicate its origin to be that considered in Part I of this paper. The case of diamond is of exceptional interest for various reasons. Its low atomic weight enables it to be used for such studies with comparatively soft X-rays without sensible loss of intensity by absorption within the crystal. Further, as it is an “ideal” crystal having a rigid lattice and a low specific heat, the effect of thermal agitation and of mosaic structure should be negligible. Diamond is therefore specially suitable for the present investigation. The simplicity of its crystal structure also facilitates the interpretation of the observed results.

Thin plates of diamond with their faces parallel to one of the octahedral cleavages of the crystal are readily obtained. The normal to an octahedral cleavage face is an axis of trigonal symmetry, and is inclined to the normals to the other three pairs of octahedral faces at the tetrahedral angle, namely $109^{\circ} 28'$. Accordingly, if a pencil of X-rays passes through such a plate normal to its faces, it is incident on the three sets of (111) crystal planes at a glancing angle of $19^{\circ} 28'$. The reflections from these planes would therefore appear in the Laue pattern as a distinct group of three spots forming an equilateral triangle which are easily recognised and identified (see figures 1 and 2 in plate I). When the crystal setting is not quite normal to the X-ray beam, the triangle appears distorted (see figures 3 and 4 in plate II). These photographs were taken with an X-ray tube having a copper anticathode and run at 41,000 volts. The beam accordingly contains the CuK_{α} and CuK_{β} rays in considerable strength, accompanied by white radiations of shorter wavelengths. When figure 1 was photographed the K_{β} radiations were cut off with a nickel foil, while figures 2, 3 and 4 were obtained, with the unfiltered radiation.

2. Experimental results

The four figures exhibit remarkable differences in the appearances of the (111) reflections (three in each figure) produced by varying the angle of incidence and (in figure 1) also by cutting off the K_β radiation. The differences consist in the shape, size and intensity of the Laue spots, the appearance of fainter companions in their vicinity, and the presence of streamers radiating at an angle from these companions (see figure 3). In order to exhibit clearly how these variations are determined by the glancing angle, eight pictures of the (111) reflections obtained with the unfiltered Cu radiation have been arranged in a vertical row in figure 5, plate III, so that the positions and intensities of the Laue spot and of its companions can be readily compared by inspection.

To appreciate the significance of the experimental results, we may remark that the (111) planes in diamond are those that give the strongest reflections and have therefore a large structure amplitude. Their spacing is 2.055 A.U. while the effective wavelengths of the CuK_α and K_β rays may be taken as 1.537 A.U. and 1.389 A.U. respectively. To obtain a Bragg reflection of the K_α and K_β radiations, therefore, the glancing angles on the (111) planes should be respectively $21^\circ 58'$ and $19^\circ 45'$. For the series of eight pictures shown in figure 5, the actual glancing angle as determined from the position of the Laue spot, and the plate distance alters from $17^\circ 10'$ for figure 5(a) to $22^\circ 13'$ for figure 5(h), thus covering a range of angles from much below to much above that required for a Bragg reflection of the K_β radiation, while in figure 5(h), the glancing angle is nearly that required to give a Bragg reflection for the K_α radiation.

From a study of these photographs, we draw the following conclusions: (1) The companion spots which accompany the Laue reflections appear in the plane of incidence of the X-ray beam on the crystal planes, that is to say, in the same plane as the Laue spots, but unlike the latter, do not satisfy the usual geometrical law of reflection from the crystal planes. (2) The two companion spots are due to the monochromatic CuK_α and K_β radiations respectively. This is shown by the fact that the inner spot vanishes when the K_β radiation is filtered out. (3) The spots are in the nature of well-defined specular reflections being, in fact, nearly as sharply defined as the usual Laue reflections of the white radiation; they tend, however, to be round instead of elliptic in shape. (4) The intensity of the spots increases rapidly as their position approaches that at which they could be identified with a regular geometric reflection from the crystal planes satisfying the usual Bragg formula. The spots continue to be however of perceptible intensity for directions removed by at least 10° on either side of such geometric reflection. (5) When a spot is at or near the position of maximum intensity, it is accompanied by streamers which do not lie in the plane of incidence but which appear to stretch towards or away from the two other (111) Laue spots.

The following table shows the measured distances of the Laue spots and of its two companions in the series of pictures figures 5(a) to (h) measured from the centre of the Laue diagram, the plate distance being 3.98 cms.

Table 1. Distances of spots from centre

Figure 5	Laue spot (cm)	Inner companion (K_β) (cm)	Outer companion (K_α) (cm)
(a)	2.72	3.13	3.55
(b)	2.85	3.20	3.60
(c)	3.04	3.22	3.65
(d)	3.31	Not separated	3.72
(e)	3.38	Not separated	3.74
(f)	3.50	3.30	3.76
(g)	3.54	3.34	3.78
(h)	3.60	3.36	3.81

The distances of a spot from the centre of the pattern for Bragg reflections of the CuK_α and CuK_β radiations respectively from the (111) spacings would be respectively 3.83 cms and 3.28 cms. It will be noticed that these distances coincide with the observed position of the spots when they are near the position of maximum intensity, but tend to deviate systematically from it in one direction or the other when they move away from this position.

3. Interpretation of the results

The general nature of the results described above leaves little doubt that we are here dealing with modified X-ray reflections of the kind discussed in Part I of the paper. We may however go a little more deeply into the matter in the light of the known crystal structure and properties of diamond.

The (111) planes have the largest spacings and give the strongest reflections amongst the crystal planes in diamond. It is therefore not surprising that they should give the modified X-ray reflections with notable intensity. The reason for this becomes clearer when we examine the nature of these spacings. As is well known, diamond consists of *two* interpenetrating face-centred cubic lattices of carbon atoms which we may refer to as the A and B lattices. The (111) spacings consist of planes of atoms belonging to lattice A interleaved by planes of atoms belonging to lattice B, the distance between the nearest layers of A and B atoms being one-fourth of the distance between the successive planes of A or of B atoms. It is this arrangement that makes the reflection from the (222) planes weak or evanescent, and makes the structure-amplitude of the (111) spacings correspondingly strong. If, now, we imagine the A and B lattices to oscillate as rigid wholes relatively to one another, the structure-amplitude of the (111) spacings should exhibit a strongly marked variation. For, the electron density between the most nearly adjacent A and B planes of atoms would increase when these planes

approach each other and *per contra*, diminish when they recede. At the same time, the electron density between the less nearly adjacent A and B planes would behave in the opposite way, that is, would diminish in one case and increase in the other. The oscillation of the two elementary lattices with respect to one another in a direction normal to an octahedral cleavage face should therefore produce a stratification of the electron density which is periodic in time and has the same spacing as the (111) planes. These planes should thus be in a position to give a modified reflection of the incident X-rays.

When a crystal of diamond is illuminated with monochromatic light, the spectrum of the scattered light exhibits a single sharp line of great intensity with a spectral shift of 1332 wave-numbers. It is a well-established result that this frequency-shift is due to the same oscillation which we have considered here, namely, a linear vibration of the two interpenetrating lattices A and B with reference to one another. The oscillation is triply degenerate, in other words, may take place in any arbitrary direction or simultaneously in different directions with arbitrary phases, the frequency being the same in every case. It is evident that the structure-amplitude of a particular (111) spacing would be influenced only if the movement of the lattices has a component normal to that spacing and would be unaffected if the movement is parallel to it. So long, however, as the two interpenetrating lattices move as rigid units and the phase of the motion is identical in all the individual cells, the periodic stratifications of electron density produced by such motion remain everywhere parallel to the respective crystal planes and have identically the same spacing as these planes. On these assumptions, therefore, the modified reflection of the X-rays by any set of crystal planes would appear only in the same direction as the ordinary Laue reflections.

Actually, as we have seen, the modified X-ray reflections associated with a particular set of the (111) planes in diamond continue to appear with practically undiminished sharpness, though with rapidly diminishing intensity, as we move away from the correct Bragg orientation for the particular X-ray wavelength. Further, as shown by the figures in table 1, if the modified reflection is regarded as a Bragg reflection from a periodic stratification of electron density inclined to the crystal spacing, not only does the effective 'structure-amplitude' of such stratifications diminish rapidly as they are tilted away from the crystal planes, but the effective spacing of such tilted wave-fronts progressively deviates from the actual crystal spacing. A glance at the figures in table 1 shows that this apparent change of spacing occurs in such a direction that the modified reflection is nearer to the direction of the Laue reflection than would otherwise be the case. These results become intelligible when we recognize that the circumstances most favourable for the modified reflection to make its appearance are precisely those in which the unmodified reflection is also obtained. In any other case, a modified reflection is only separable from the unmodified reflection if the oscillation of the structure-amplitude departs from the ideal condition of having the same phase everywhere. A diminution of the intensity of the resulting reflection is only to be expected in such circumstances.

Empirically, it is found that the formula

$$\lambda^* \sin(\theta + \phi) = \lambda \cos \phi, \quad (1)$$

nearly fits the results for diamond shown in table 1. Here θ , ϕ are the glancing angles of incidence and reflection with respect to the crystal planes, λ^* is the spacing of the latter, and λ the X-ray wavelength. It will be noticed that the formula is unsymmetrical in θ and ϕ , in other words, they are not interchangeable. On the other hand, a formula of the symmetrical type

$$2\lambda^* \sin \frac{1}{2}(\theta + \phi^*) = \lambda \quad (2)$$

for the modified reflection would make it completely analogous to the Bragg formula and give an angular separation $(\theta + \phi^*)$ of the incident X-ray beam and of the modified reflection which is the same for all orientations of the crystal and therefore identical with that for the unmodified reflection. Comparing (1) and (2), it is easily seen that

$$\begin{aligned} \text{If } \phi > \theta, & \quad \text{then } \phi < \phi^* \\ \text{If } \phi < \theta, & \quad \text{then } \phi > \phi^*. \end{aligned}$$

This is what the figures given in table 1 indicate. Both the formulae (1) and (2) reduce to the Bragg formula when $\theta = \phi$ or ϕ^* .

We may now remark on the explanation of the oblique streamers [seen in figure 3 and figure 5(h)] which as already mentioned, accompany the modified X-ray reflection in diamond when it is of sufficient intensity. It will be noticed that they radiate towards or away from the two other Laue spots due to the (111) spacings, instead of towards the centre of the pattern. Their explanation is to be found in the fact already remarked that the lattice oscillation in diamond is triply degenerate, and may therefore co-exist in different directions and in different phases. In general, therefore, variations of the structure factor of each of the three sets of (111) planes would occur simultaneously. An X-ray beam incident on any one set of these planes and reflected by it would also be influenced by the stratifications having the same spacing and frequency parallel to the two other sets of these planes. The streamers accompanying the modified reflection are evidently secondary effects due to the superposition of the three sets of stratifications. This is clearly shown by the directions which they assume.

The radial streamers which stretch from the Laue reflection towards the centre of the pattern have a different origin. They are best seen with diamond when the modified reflections due to the K_α and K_β rays both lie outside the Laue spot, and may therefore be identified with the modified reflection of the *white* radiations of shorter wavelengths present in the incident X-ray beam.

4. Significance of the diffuse halo

Referring again to figures 1, 2, 3 and 4 in the plates, a very striking feature of these Laue patterns is the strong though diffuse halo which appears surrounding the

primary X-ray beam. Its outer limit is ill-defined, and indeed towards its periphery the halo mingles insensibly with the diffuse scattering by the crystal which overlays the entire Laue pattern. It is, however, evident that the intensity of the halo is relatively great over a limited area which lies well within the triangle formed by the (111) Laue spots. That the phenomenon is really due to the diamond has been fully established by blank exposures without the crystal which give a clear film except over a narrow ring due to the primary beam surrounding the blocked-out circle at the centre. Allowing for this narrow ring, it appears that the maximum intensity of the halo is not at the centre of the pattern, but very definitely further out, in fact about half-way between the centre and the (111) Laue spots. In well-exposed pictures, the falling off in the intensity of the halo towards its centre is clearly seen. In considering the origin of the halo, we must, of course, take into account the composition of the incident X-radiations, which includes besides the CuK_α and K_β rays, also a considerable intensity of white radiation of shorter wavelengths. The elimination of the latter, if it had been possible, would undoubtedly have accentuated the falling off in intensity of the halo towards the centre of the pattern and made the existence of a well-defined maximum at a distance from the centre more strikingly evident. There can be little doubt, however, that the most intense region of the halo owes its origin to the monochromatic K_α and K_β radiations of the copper anticathode.

It will be remembered that in Part I of the paper, we have referred to Brillouin's theory of the reflection of monochromatic X-rays by sound-waves of thermal origin. This theory indicates the appearance of a continuous diffusion halo in the X-ray pattern extending from the centre outwards and falling off in intensity to zero at an angle corresponding to the short wavelength limit of the acoustic spectrum. Brillouin's expression for the intensity of the halo includes a Planck factor which is equal to unity for the lowest frequencies and tends to zero for acoustic frequencies for which $h\nu \gg KT$. Accordingly, for the case of diamond, the intensity of the Brillouin halo should be vanishingly small except very near its centre. Actually, as is evident from the photographs, the halo is a conspicuous phenomenon and exhibits a maximum at an angular radius from the centre of about 20° . It is therefore clear that though the halo is evidently due to the reflection of the X-rays by acoustic waves as postulated by Brillouin, its intensity is much larger than that indicated by his theory. The basic idea of his theory, namely, that the sound-waves responsible for the scattering of X-rays are of thermal origin, cannot therefore be accepted. If, however, we consider the acoustic waves to be actually excited by the X-ray quanta, the difficulty would disappear, as the intensity of the scattering would then be vastly greater and in better accord with the observed facts. The distinct concentration of the scattering in a ring-shaped halo suggests that the acoustic spectrum has a marked intensity maximum at a wavelength roughly about double the shortest permissible.

We must not, of course, omit to mention the Compton scattering. Theory indicates that this is of zero intensity for the forward scattering and increases to its full value at large angles. In the case of diamond, the Compton scattering is

probably responsible for most of the radiation diffused by the crystal through large angles. Nearer the centre of the pattern, however where the intense diffuse halo is observed, the Compton scattering is less important, and the observed effect is mostly due, as we have seen, to the acoustic waves excited by the incidence of the X-radiation.

5. Influence of temperature

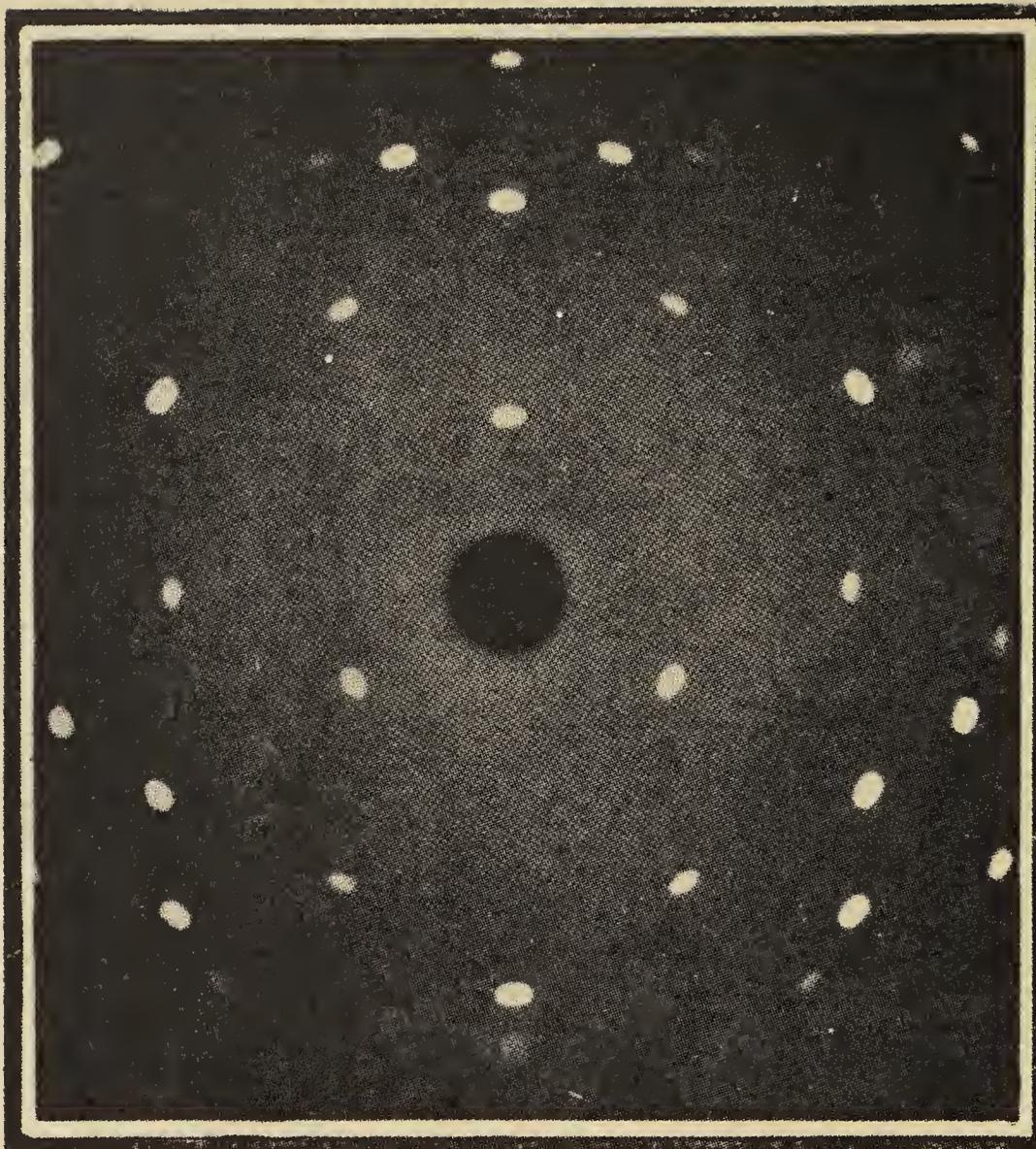
As explained earlier in the paper, the choice fell on diamond as the crystal for these experiments, mainly because phenomena of purely thermal origin would, *prima facie*, be negligible in dealing with it. This is evident when we consider the magnitude of the Planck factor $1/(\exp(h\nu/KT) - 1)$ which indicates the extent of thermal excitation of any oscillation of frequency ν . At room temperature ($T = 300^\circ$), $h\nu = KT$ for a frequency $\approx 6 \times 10^{12}$, whereas the characteristic frequency of diamond corresponding to 1332 cm^{-1} is 40×10^{12} . The magnitude of the Planck factor for this frequency is entirely negligible, while it is small even for a frequency which is only half of it. The appearance of a modified X-ray reflection due to the lattice oscillation in diamond and indeed also of the scattering by the acoustic waves for lower frequency must therefore be regarded as quantum effects. A very convincing demonstration that this is the case would be to cool down the diamond to liquid air temperatures and to observe whether the effects under consideration persist undiminished, as is to be expected. Experiments of this kind are in progress and will be reported as soon as they are completed. As corresponding experiments with light show that modified scattering persists with undiminished intensity at the lowest temperatures, we may confidently anticipate an analogous result also with modified X-ray reflection at angles close to the usual Laue reflections. The falling off in the intensity of the modified reflection when the crystal is tilted away from the correct position for a Bragg reflection may however conceivably show a more marked temperature dependence. This is a matter for further investigation.

In the case of the modified scattering of light, the intensities of the Stokes and anti-Stokes components are respectively proportional to $1/(1 - \exp(-h\nu/KT))$ and $1/(\exp(h\nu/KT) - 1)$. The first of these quantities is approximately independent of temperature so long as $h\nu \gg KT$. For a characteristic frequency 40×10^{12} , the temperature dependence of the intensity of the Stokes component should only become sensible when $T > 1000^\circ$. Investigations on light scattering in diamond made recently at Bangal re show that when the crystal is heated, it exhibits an appreciable alteration of the characteristic frequency, and it is probable also that at higher temperatures the frequency broadens out into a band. Accordingly, we should not be surprised to find in the X-ray phenomena temperature effects more pronounced than those indicated by the formula quoted.

Photographs of the Laue pattern of diamond at 25° C and at 500° C show at the

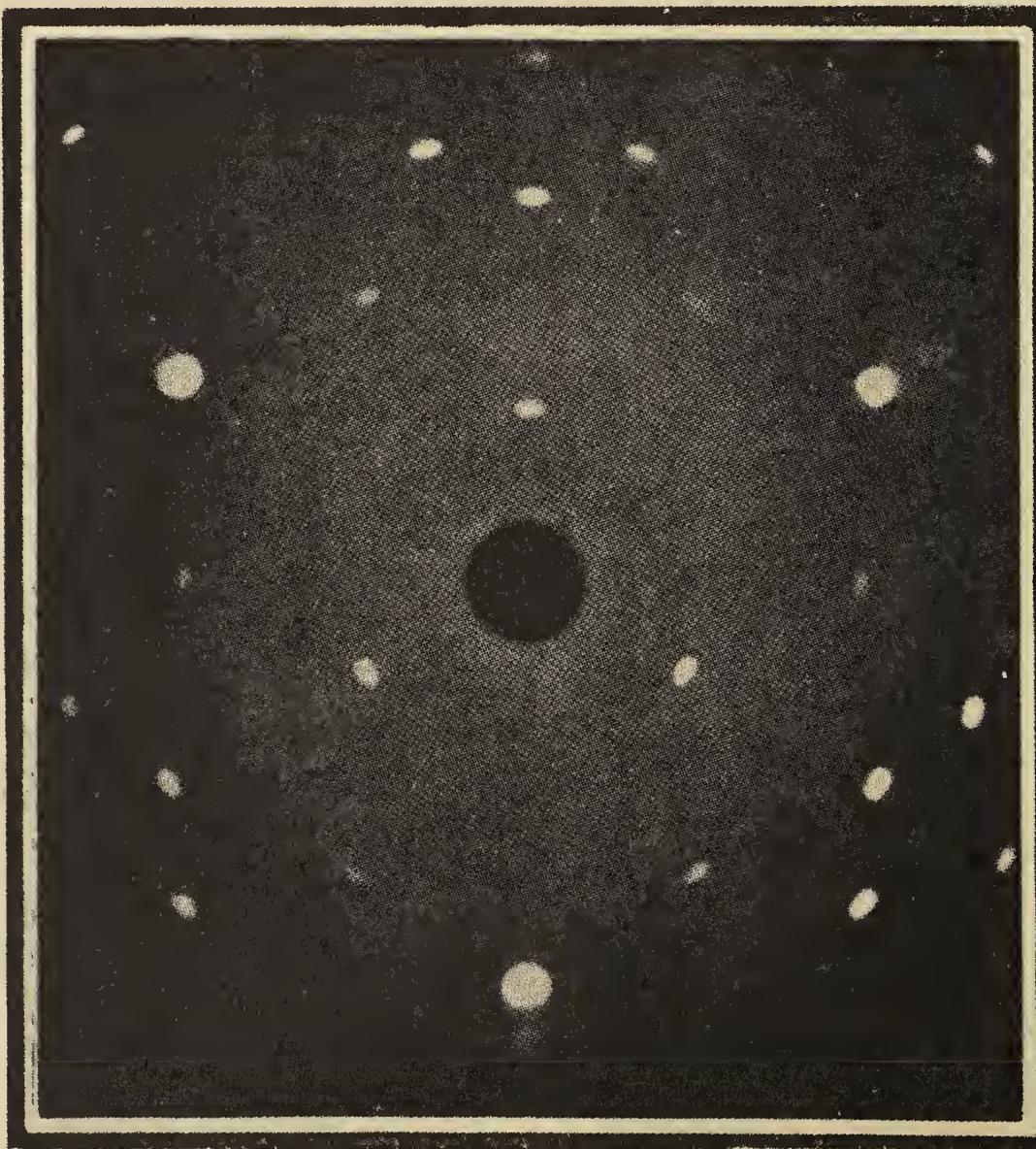
higher temperature a slight enfeeblement of the ordinary Laue reflections, and a detectable but not very striking enhancement of the intensity of the modified reflections, as also of the diffuse halo appearing in the pattern. The thermal expansion of the crystal with consequent shifting of the relative positions of the Laue and modified reflections however complicates the issue, as the intensity of the modified reflections depends greatly on their relative position. A more detailed study is therefore necessary before any definite conclusions can be drawn. Nevertheless, the observations so far as they go indicate pretty clearly that the modified reflection of X-rays and the diffuse halo are not *primarily* thermal phenomena. This statement, it will be noticed, does not exclude observable thermal influences on the phenomena, such as sharpening of the reflections at low temperatures, or their brightening up and becoming more diffuse at high temperatures.

(1)



Filtered,
 CuK_α
radiation
only

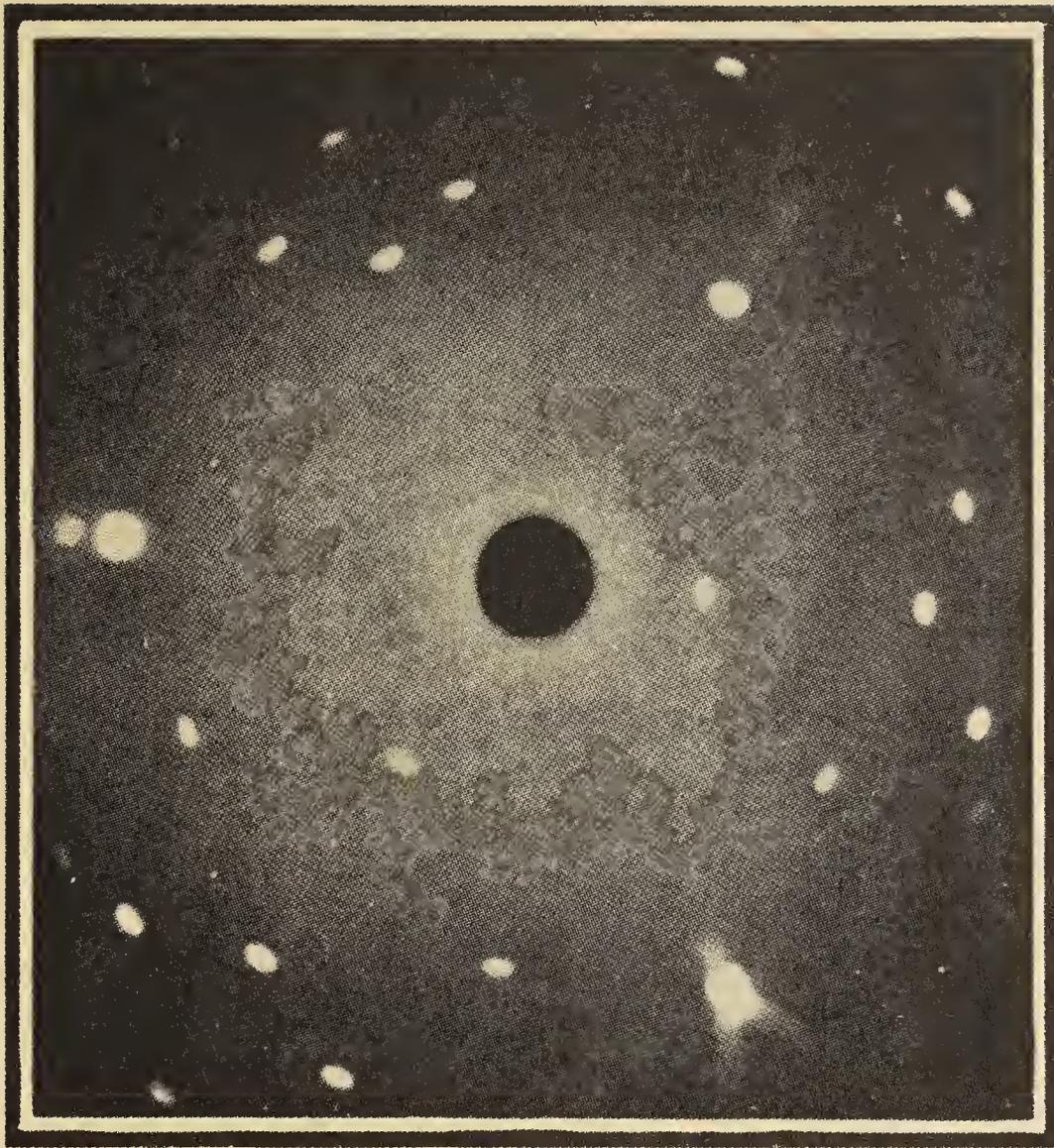
(2)



Unfiltered.
 CuK_α
and CuK_β
radiation

Figures 1 and 2. Symmetrical Laue pattern of diamond (normal to cleavage plane).

(3)



(4)



Figures 3 and 4. Asymmetrical Laue pattern of diamond (approximately normal to cleavage plane).

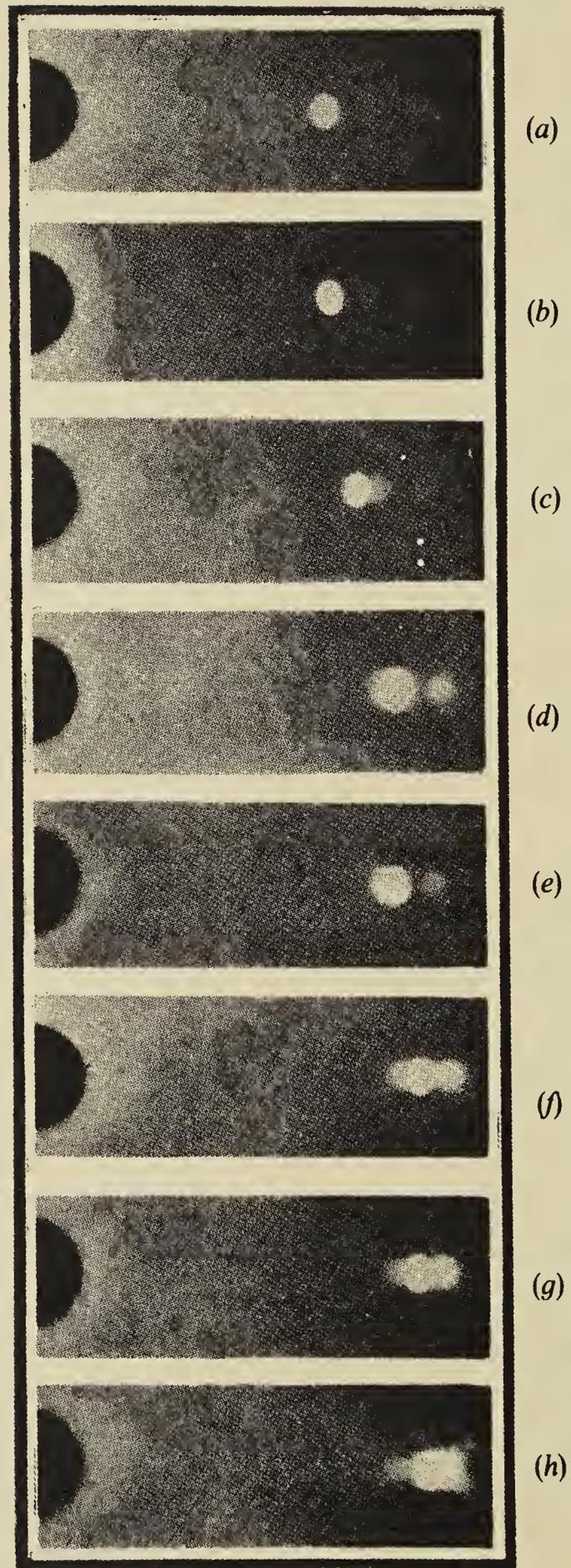


Figure 5. Showing Laue spot due to reflection from $[111]$ planes of diamond and modified reflections due to K_α and K_β radiations.

Reflection of X-rays with change of frequency— Part III. The case of sodium nitrate

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1. Introduction

Sodium nitrate is very similar in crystalline form and structure to calcite, but owing to the lower atomic weight of sodium, is better suited than calcite for X-ray studies with a copper-target tube. Its physical properties present a striking contrast with those of diamond. The melting point of the crystal is 309.5°C , indicating that its characteristic frequencies are low. The unit cell contains two ions of Na and two of NO_3 situated along the trigonal axis of symmetry. There are thus ten atoms in the cell occupying non-equivalent positions, and the possible modes of oscillation of the interpenetrating lattices are therefore numerous. Theory indicates that there should be eighteen fundamental frequencies of vibration, nine of them being doubly degenerate. Ten of these fundamentals should have low frequencies representing translatory movements of the Na and NO_3 ions and rotational oscillations of the latter. The remaining eight fundamentals should have high frequencies corresponding to the internal vibrations of the NO_3 ions. Actually, the crystal exhibits two low and three high frequencies in light-scattering, while in infra-red absorption, three low and three high frequencies have been observed, all these being different. Three low and two high frequencies are theoretically forbidden from appearing either in light-scattering or in infra-red absorption. The agreement with theory is thus nearly complete. Diagrams illustrating the different possible modes of oscillation will be found in a recent paper by Bhagavantam and Venkatarayudu (1939). Nedungadi (1939*a*) has studied in considerable detail, the influence of temperature on the spectrum of light-scattering in sodium nitrate, and has found that the two low frequency lines with wave-number shifts 98 and 185 are displaced to still lower frequencies and broaden greatly when the crystal is heated above 180°C , finally becoming diffuse bands as the melting point is approached. Nedungadi (1939*b*) has also identified the modes of vibration corresponding to these low frequencies by studies of the polarisation of light-scattering in orientated crystals.

The planes in the crystal structure parallel to the rhombohedral cleavages give

by far the most intense X-ray reflections. As in the case of diamond, therefore, we should expect these planes also to give intense modified reflections. The diagonal planes passing through the edges of the cleavage rhomb and bisecting the acute angle between its faces also give intense Bragg reflections, and by the same token should give strong modified reflections. The crystal planes normal to the trigonal axis of symmetry consist of alternate layers of Na and NO_3 ions. The reflections due to these planes are not very strong. In view, however, of the fact that several of the fundamental modes of vibration consist of movements of the Na and NO_3 ions along the axis of symmetry, marked variations of the structure-amplitude of these planes may be expected. We may therefore reasonably anticipate that these planes should give modified reflections with notable intensity.

Remarkable changes are observed in the intensity of the rings in the X-ray powder pattern of sodium nitrate when the temperature is raised above 180°C and up to a little below its melting point. These changes have been very fully studied by Kracek and co-workers (1931), whose results have been confirmed by Nedungadi at this Institute. The most interesting feature is that above 180°C , the rise of temperature affects the intensity of the X-ray reflections due to different spacings very unequally. Some are scarcely affected, some reflections diminish in intensity a little, while a few which are fairly strong below 180°C are practically wiped out when the temperature rises towards 250°C . It thus appears that the structure-amplitude of some of the spacings is very markedly a function of temperature in this range. Kracek and his co-workers have suggested that this is due to the rotational oscillations of the NO_3 ions gradually increasing in amplitude and passing into continuous rotation in the temperature range from 180°C to 290°C . It may be mentioned that this is also the temperature range in which Nedungadi finds that the low frequency lines observed in light scattering broaden out and shift to lower frequencies.

To bring out the position clearly, we give below in table 1, a list of the principal planes and crystal spacings in sodium nitrate, and the intensities of the X-ray reflections due to them (on an arbitrary scale) as given by Kracek *et al.*, at 25°C and at 280°C .

The Millerian indices of the planes given in the first column of the table have reference to the axes of the elongated rhombohedron which is the unit cell of the crystal lattice. In this notation, (211) represents a cleavage face, (323) is a diagonal plane bisecting the acute angle between the cleavage faces and (222) is normal to the trigonal axis. It will be noticed from the table that the (211) and (323) planes give strong reflections which are scarcely influenced by temperature, while the (222) planes give a weaker reflection which falls off appreciably on heating. The (210) planes are specially remarkable as they give a strong reflection which disappears at high temperatures. The last column in the table indicates the manner in which the structure-amplitude of the respective planes is effectively determined by the contributions of the three species of atoms in the crystal, according to Kracek and his co-workers.

Table 1. Crystal spacings in sodium nitrate

Indices	Spacing Å at 25° C	Spacing Å at 280° C	Intensity at 25° C	Intensity at 275° C	Structure- amplitude
110	3.902	3.921	2	3	N + O - Na
211	3.035	3.121	> 10	> 10	N + O + Na
222	2.802	2.932	4	2.5	N + O - Na
1 $\bar{1}$ 0	2.534	2.543	3	3.4	N + O + Na
210	2.310	2.313	6	< 0.5	O
		at 250° C			
200	2.122	2.138	4	2.4	N + O - Na
220	1.943	1.964	1	7.7	N + O + Na
323	1.893				7
321	1.880	1.914	3	2.2	N + O - Na
2 $\bar{1}$ 0	1.649	—	3	< 0.5	O
2 $\bar{1}$ 1	1.626	1.637	2	1.2	N + O - Na

2. Experimental results

Figures 1 and 2 in plate I, figures 3 and 4 in plate II, figures 5 and 6 in plate III, figures 7 and 8 in plate IV, figures 9 and 10 in plate V are Laue patterns of sodium nitrate obtained with the unfiltered radiation from a copper target. They illustrate the phenomena exhibited by this crystal in various circumstances. Figures 1, 2, 3, 4, 5 and 6 show the modified reflections by some of the principal planes at various angles of incidence, while figures 7, 8, 9 and 10 exhibit the effect of raising the temperature from 25° C successively to 200°, 225° and 275° C, the position of the crystal remaining unaltered.

In obtaining all these photographs, the crystal was placed with one of its cleavage faces in a vertical plane, the longer diagonal of this face being vertical. The incident X-ray beam passed through the cleavage face in a horizontal direction, and its angle of incidence on the various crystal planes could be altered by rotating the crystal about the vertical diagonal. In all the settings of the crystal, the trigonal axis of the crystal remained horizontal, its inclination to the X-ray beam being varied. The Laue patterns accordingly exhibit two-fold symmetry about a horizontal axis. The two other cleavage faces of the crystal being inclined to the vertical, the reflections from them appear in two directions symmetrically inclined to the horizontal. The (222) and (323) planes being always vertical, the reflections from them appear on the horizontal axis of the pattern in suitable settings of the crystal.

The most conspicuous features in figures 1, 2, 3 and 4 besides the usual Laue spots, are the modified reflections from the two cleavage planes. In figures 2 and 3, the K_α and K_β modified reflections appear as distinct spots adjacent to the Laue

reflections from the same planes, while the modified reflections of the white radiation appear as radial streaks stretching towards the centre of the pattern and distinctly separated from the K_α and K_β reflections. In figures 1 and 4, the Laue reflections are far removed from the modified reflections of the K_α and K_β rays in one direction or the other; but the latter continue to be visible in approximately the same positions as in figures 2 and 3, though only as diffuse spots or clouds. The radial streaks are also seen in approximately the same positions. That the latter are due to the modified reflection of the white radiation will be very evident on comparing figures 1 and 4. When the Laue spots are nearer the centre of the pattern than the modified reflections of the K_α and K_β radiations, they are traversed by the radial streaks, whereas when the Laue spots are further away, they are not overlaid by the streaks.

The inclination of the X-ray beam to the trigonal axis of the crystal in figures 1, 2, 3 and 4 was successively 56° , 50° , 44° and 39° . It is a notable fact that the modified reflections from the cleavage planes continue to be visible in spite of the large change in the angle of incidence which is indicated by the displacement of the Laue reflection from near the centre of the photograph to near its outer margin. On comparing figures 2 and 3, the great increase in the intensity of the modified reflection of the K_α radiation when it approaches the Laue spot will be evident. This phenomenon has already been noted in the case of diamond. It is evident, however, that the modified reflections are more conspicuous in intensity and observable over a wider range of incidences in sodium nitrate than in diamond. They are also somewhat more diffuse than is the case with diamond.

In obtaining the Laue patterns reproduced as figures 5 and 6, the crystal was turned over by 180° about the vertical diagonal. This made it possible to get the reflections from the (222) planes to the left of the pattern simultaneously with those from the (211) and the (323) planes on its right. A slightly smaller plate distance was also used. The modified reflection of the K_α radiation from the (222) planes is clearly seen in figures 5 and 6 to the right and left of the Laue spots respectively, the actual glancing angle of the beam on this plane in the two photographs being 18° and 11° , being thus respectively greater and less than the Bragg angle of $15^\circ 55'$. The spacing of the (323) planes being 1.893 \AA , the Bragg angle for these planes and the K_α radiation is $23^\circ 57'$. This being much greater than the actual glancing angle in either of the two patterns, we do not observe the modified reflection of the K_α and K_β radiations from the (323) planes but only those of the white radiations of shorter wavelength. These appear as intense horizontal streaks passing through the Laue reflections. It is obvious that the modified reflection of monochromatic rays by a particular set of crystal planes cannot be observed if the wavelength of the rays used is too great to give a Bragg reflection, or if the glancing angle differs too largely from that required for such reflection. In such cases, however, if the white radiation present in the X-ray beam is sufficiently intense, its modified reflection may be observed as a radial streak passing through the Laue spot. Numerous examples of this may be seen in the photographs reproduced.

3. Geometry of modified reflection

In Part II of the paper, it was mentioned that an empirical formula of an unsymmetrical type fitted the observations with diamond, namely,

$$d \sin(\theta + \phi) = \lambda \cos \phi \quad (1)$$

θ and ϕ being the glancing angles of incidence and of modified reflection and d the crystal spacing. An alternative formula was also given which is symmetrical in θ and ϕ , namely,

$$2d \sin \frac{1}{2}(\theta + \phi) = \lambda. \quad (2)$$

This formula would have a theoretical basis if it be assumed that as the wave-fronts of the stratification giving the modified reflections tilt round, they maintain the same spacing as the crystal planes of which they are the structure-amplitude fluctuations. In table 2 are collected the values of θ and ϕ as given by the observed positions of the Laue spot and of the modified reflection, the spacing d as calculated from formulae (1) and (2), and as known from the crystal structure. The data refer to the crystal at room temperature.

Table 2. Modified reflections by sodium nitrate (211) planes: crystal spacing = 3.035 A.U. (The symbol α indicates K_α reflection; β indicates K_β reflection)

Character of reflection	Glancing angle		Spacing calculated from formula (1) in A.U.	Spacing calculated from formula (2) in A.U.
	Incidence θ	Reflection ϕ		
Very diffuse	5° 24'	23° 44' α	2.896	3.060
„	6° 20'	22° 48' α	2.942	3.090
„	6° 44'	22° 26' α	2.920	3.056
„	7° 48'	21° 22' α	2.944	3.056
Diffuse	10° 27'	18° 58' α	2.966	3.029
		15° 33' β	3.055	3.031
„	11° 34'	17° 46' α	2.994	3.040
		14° 57' β	3.007	3.092
Fairly sharp	11° 6'	18° 19' α	2.975	3.029
		15° 22' β	3.007	3.035
„	11° 50'	17° 20' α	3.016	3.056
		14° 38' β	3.017	3.035
Sharp	15° 52'	13° 28' α	3.057	3.040
		10° 36' β	3.064	3.035
„	15° 58'	13° 17' α	3.065	3.046
		10° 20' β	3.084	3.054
Very diffuse	19° 58'	9° 12' α	3.085	3.022
„	20° 47'	8° 23' α	3.092	3.022

Tables 2 and 3 include the data for the modified reflections observed in all the six Laue patterns and the corresponding spacings. It is clear from the figures that the experimental results for sodium nitrate fit the symmetrical formula (2) very well, and that the unsymmetrical formula (1) is not applicable in the case of this crystal. The figures for the (111) spacing in diamond given in Part II are compiled in table 4 in the same way as for sodium nitrate. It is clear that the experimental data for diamond agree better with the unsymmetrical formula (1) though even here there is a systematic deviation. The symmetrical formula (2) is evidently inapplicable in the case of diamond.

Table 3. Modified reflections by sodium nitrate

Glancing angle		Spacing calculated from formula (1) in A.U.	Spacing calculated from formula (2) in A.U.
Incidence θ	Reflection ϕ		
(222) Planes: crystal spacing = 2.802 A.U.			
11° 50'	20° 48' α	2.669	2.739
	17° 29' β	2.707	2.740
18° 29'	14° 1' α	2.779	2.750
	10° 50' β	2.787	2.740
(210) Planes: crystal spacing = 2.310 A.U.			
18° 12'	20° 29' α	2.307	2.325
	16° 41' β	2.327	2.317
19° 17'	19° 57' α	2.289	2.292
	15° 36' β	2.340	2.317
(200) Planes: crystal spacing = 2.122 A.U.			
21° 51'	20° 27' α	2.144	2.132
22° 31'	20° 8' α	2.133	2.115

It is remarkable that the geometric law of the modified reflections should differ so markedly with the two different crystals. It is, of course, not possible to generalise on the evidence of these two cases only. But it is permissible to suggest that these and other differences already noticed between the cases of diamond and sodium nitrate are connected with the great difference in their crystal structure and properties, and especially with the fact that diamond has a very high characteristic frequency, while sodium nitrate has numerous low frequencies and is therefore influenced to a far greater extent by thermal agitation. There is also the possibility that there may be a difference in the behaviour of "ideal" crystals and of those with a "mosaic structure". Diamond almost certainly belongs to the first class, and sodium nitrate probably to the second. The

Table 4. Modified reflections by diamond (111) planes: crystal spacing = 2.056 A.U. (The symbol α indicates K_α reflection; β indicates K_β reflection)

Glancing angle		Spacing calculated from formula (1) in A.U.	Spacing calculated from formula (2) in A.U.
Incidence θ	Reflection ϕ		
17° 11'	24° 33' α	2.104	2.161
	21° 0' β	2.098	2.123
17° 48'	24° 24' α	2.086	2.142
	21° 0' β	2.070	2.091
18° 41'	23° 50' α	2.084	2.122
	20° 18' β	2.071	2.081
19° 53'	23° 12' α	2.070	2.094
20° 10'	23° 2' α	2.069	2.090
20° 40'	22° 43' α	2.067	2.080
20° 49'	22° 43' α	2.062	2.073
	19° 11' β	2.041	2.031
21° 4'	22° 41' α	2.052	2.065
	19° 6' β	2.034	2.023

pulsations of structure-amplitude could scarcely be expected to be coherent as between consecutive units in a "mosaic" structure, while in an ideal crystal, a strict coherence of phase might well be possible. Until the intensity problem for the modified reflection of X-rays is fully worked out, however, it would be premature to discuss the probable influence of mosaic structure on the results.

4. Influence of temperature

The series of four photographs (figures 7, 8, 9 and 10) reproduced in plates 4 and 5 exhibit the effect of heating the crystal from 25° C to 200° C, 225° C and 275° C respectively. It will be noticed that as the crystal is heated, the separation between the Laue and K_α modified reflections diminishes, until at 275° C they are superposed on each other. This naturally involves a large increase in the intensity of the modified reflections of both the K_α and K_β radiations. Apart from this incidental circumstance which is due to thermal expansion, we notice the following interesting effects:

- (1) There is a marked increase in the intensity of the modified reflection of the white radiation from all the planes in the crystal, including the (211) planes.
- (2) While there is a distinct diminution in the intensity of all the Laue spots, the changes in their *relative intensity* are extremely conspicuous. Indeed, on a

careful comparison, it will be seen that some spots which are larger and brighter than others at 25° C have become much feebler or almost disappeared at 275° C.

- (3) Figure 10 shows four *faint* Laue spots which are accompanied by *strong* modified reflections, while in figure 7, the same Laue spots are intense but the modified reflections are invisible. Figures 8 and 9 show a progressive *diminution* in the intensity of these Laue spots and a progressive *increase* in the intensity of the modified reflections accompanying them. These spots have been identified from their positions as due to the (210) planes.

On a reference to table 1, it will be noticed that the (210) planes give strong Bragg reflections at 25° C, but the intensity of these reflections falls to a very small value at 280° C. We have thus *the very interesting result that the planes of which the structure-amplitude falls to zero with rising temperatures show simultaneously a large increase in the intensity of the modified reflection.*

So far from being surprising, these results are entirely in accord with the general ideas developed in Part I. The variations of structure-amplitude produced by the lattice vibrations determine the intensity of the modified reflections. In the limiting case when the thermal agitation is negligible, the lattice oscillations are themselves to be regarded as excited by the incident radiation, the modified reflection being then a pure quantum effect. With rise of temperature, however, the thermal excitation of the lattice vibrations begins to assume importance, especially when, as in the case of sodium nitrate, these are of sufficiently low frequency. The dynamic part of the structure-amplitudes would increase progressively and even rapidly, and the intensity of the modified reflection would show a corresponding increase. It must be remembered in this connection that the static and dynamic structure-amplitudes cannot be regarded as completely independent of each other. For an infinitesimal disturbance of the lattice it might be correct to regard the dynamic variation of the structure-amplitude as superposed on the static structure-amplitude without sensibly influencing it. This would however cease to be true when the amplitudes of vibration are finite. The actual influence of the vibration on the static structure-amplitude would naturally depend on the circumstances of each case. Broadly speaking, however, it may be said that with increasing amplitude of vibration, the static structure-amplitudes would diminish and the dynamic amplitudes would increase, the two effects being closely correlated. In other words, with rise of temperature, the unmodified or Laue reflection would diminish in intensity, and the modified reflections would correspondingly become more intense. It is thus clear that the modified reflection of X-rays plays a very important role in the theory of the temperature effect in X-ray diffraction. This is particularly well brought out by the case of the (210) planes in sodium nitrate which, as we have seen, show a static structure-amplitude tending to zero with rise of temperature and a dynamic structure-amplitude rising to a correspondingly high value.

Summary of parts I, II and III

These papers deal with a new type of X-ray reflection in crystals which is dynamic in character and thus differs from the static reflections of the Laue type.

Part I considers the broad theoretical aspects. The optical analogy of the scattering of light in crystals indicates that when X-rays traverse a crystal they excite pulsations in the crystal lattice having the characteristic infra-red frequencies, and these pulsations in turn cause periodic variations in the structure-amplitude of the crystal spacings and therefore result in reflections of the X-rays with change of frequency. At the Bragg angle of incidence, the modified and unmodified reflections are superposed, but when the incidence is increased or decreased, the unmodified reflections disappear, thus enabling the modified reflections to be observed by themselves. They are seen in the plane of incidence on the crystal spacing, but at an angle greater or less than that of geometric reflection by the crystal planes. The modified reflection is a quantum effect and is not primarily a thermal phenomenon, though for low lattice frequencies or at high temperatures it may be thermally influenced.

Part II describes the experimental results obtained by the study of the modified reflection from the (111) planes in diamond. The lattice vibration which is effective is that characteristic of the crystal which also appears in light-scattering with a frequency of 1332 cm^{-1} . This is confirmed by the character of the effects as described in detail.

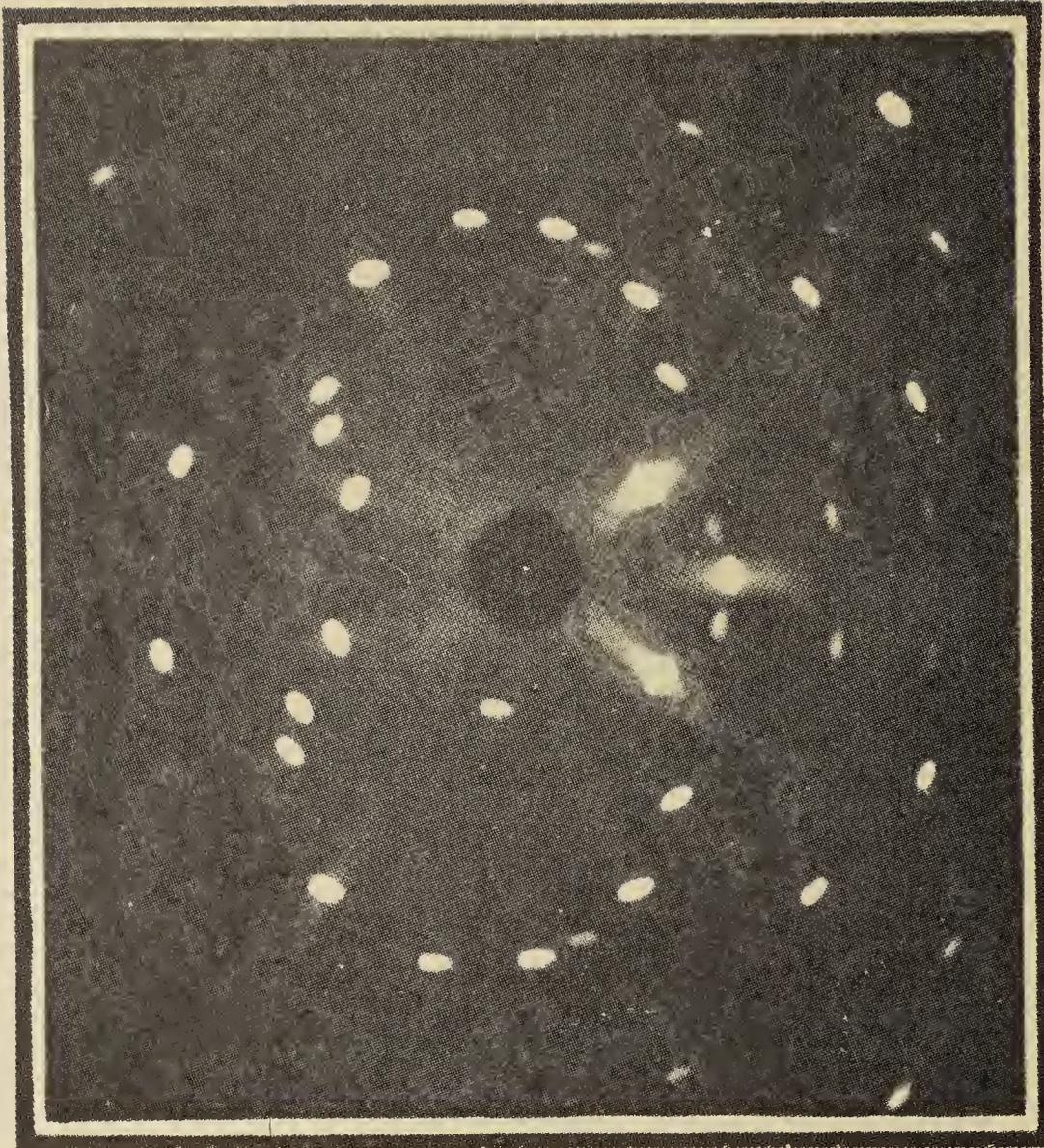
Diamond exhibits a diffuse halo with a distinct darkening at the centre of the pattern and a maximum of intensity at a distance from it. This is explained as due to acoustic waves of high frequency excited by the incident monochromatic X-rays and reflecting them in the usual way.

Part III describes the results obtained with sodium nitrate which exhibits intense modified reflection by several of the crystal spacings. The geometric law of modified reflection is discussed in relation to the experimental data for both crystals. A study of the temperature effects observed with sodium nitrate indicates that a diminution in the intensity of the unmodified reflection is accompanied by an increase in the intensity of the modified reflection. The modified reflections therefore play an important point in the theory of the temperature effect in X-ray diffraction.

References

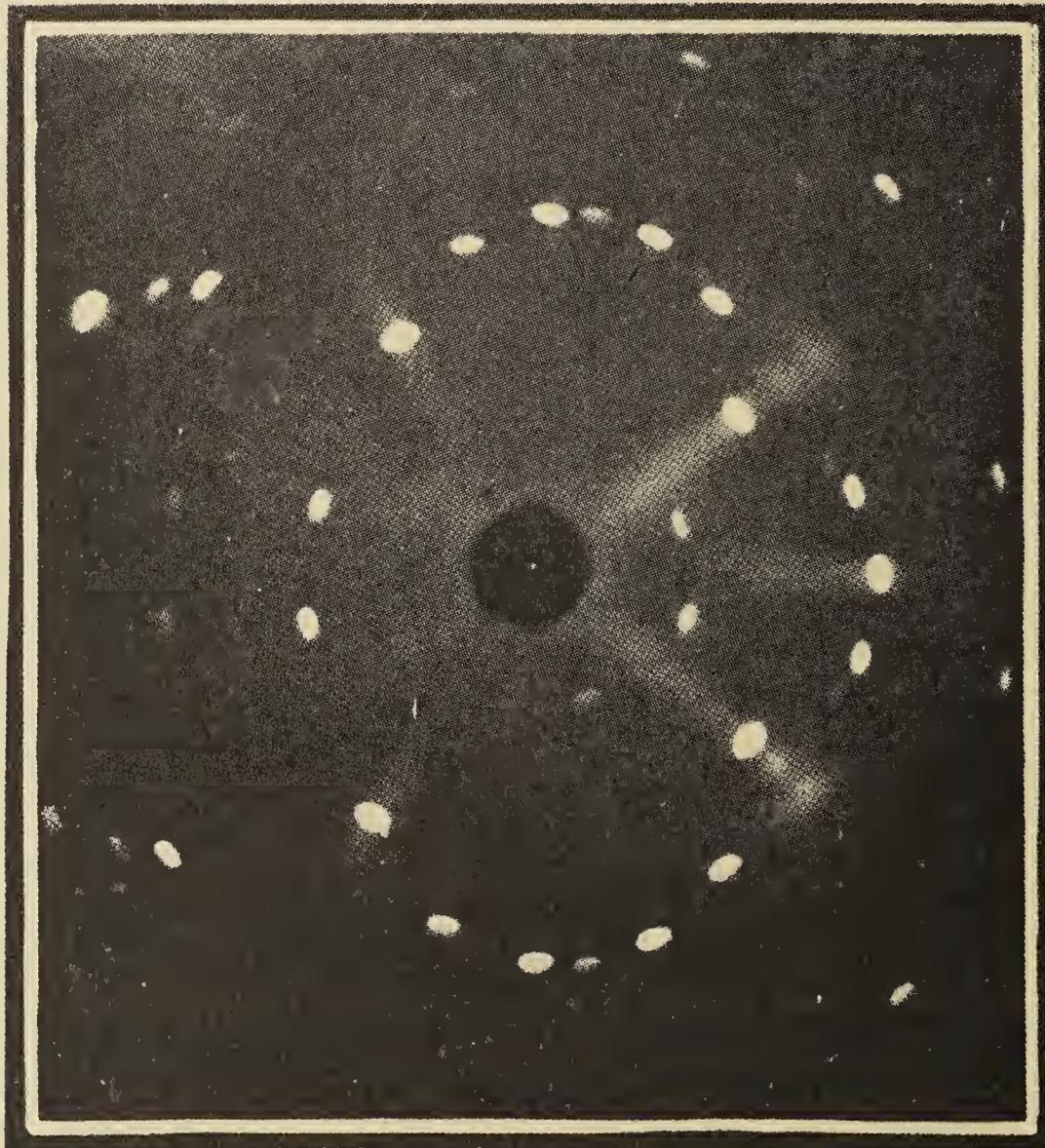
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Nedungadi T M K *ibid.* **8** 397 (1938); **10** 195 (1940).
Kracek, Posnjak and Hendricks *J. Am. Chem. Soc.* **53** 3339 (1931).

(1)



X-ray beam
inclined 56°
to the
trigonal
axis

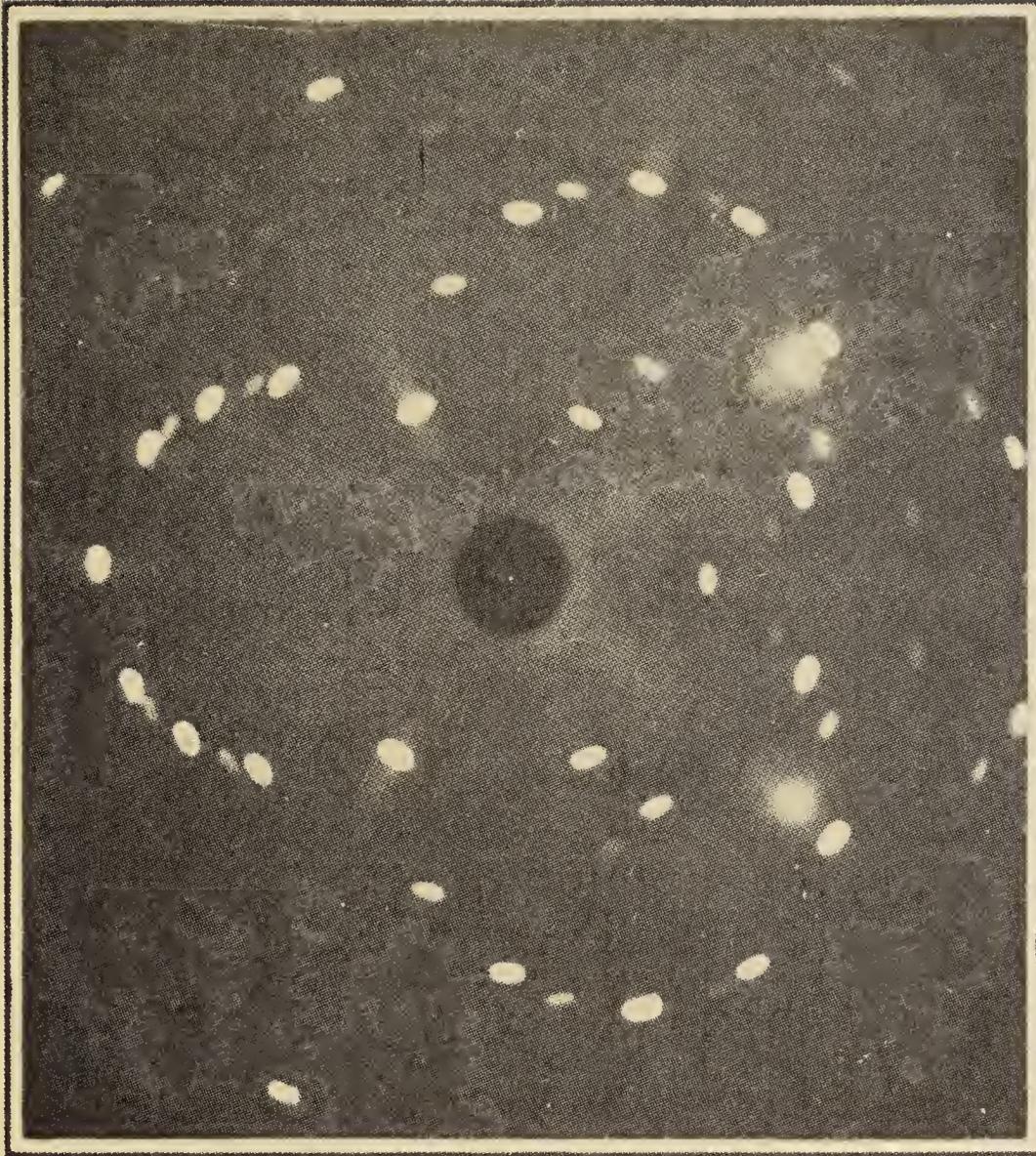
(2)



X-ray beam
inclined 50°
to the
trigonal
axis

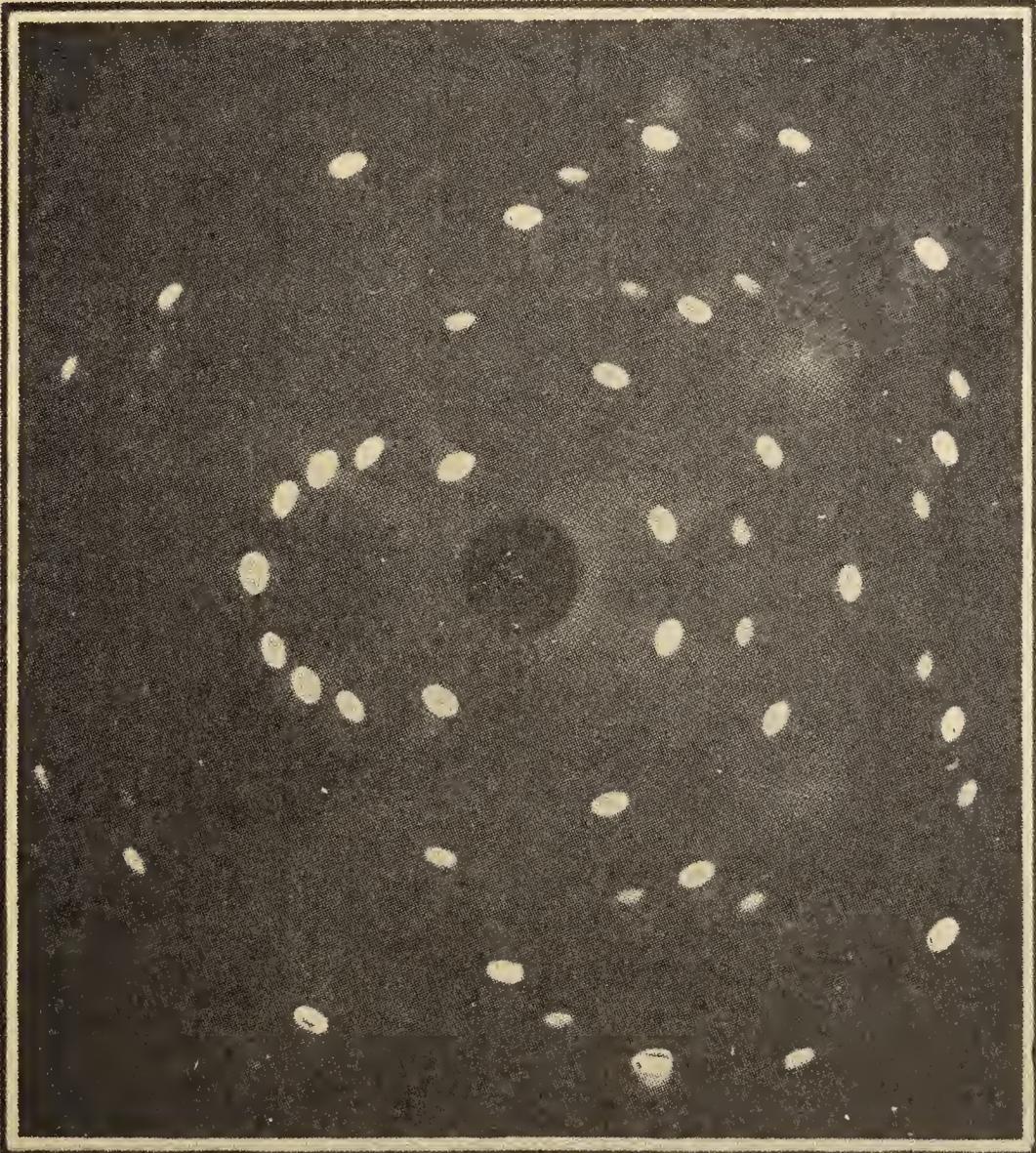
Figures 1 and 2. Laue pattern of sodium nitrate (trigonal axis horizontal).
Plate I

(3)



X-ray beam
inclined
 44° to the
trigonal
axis

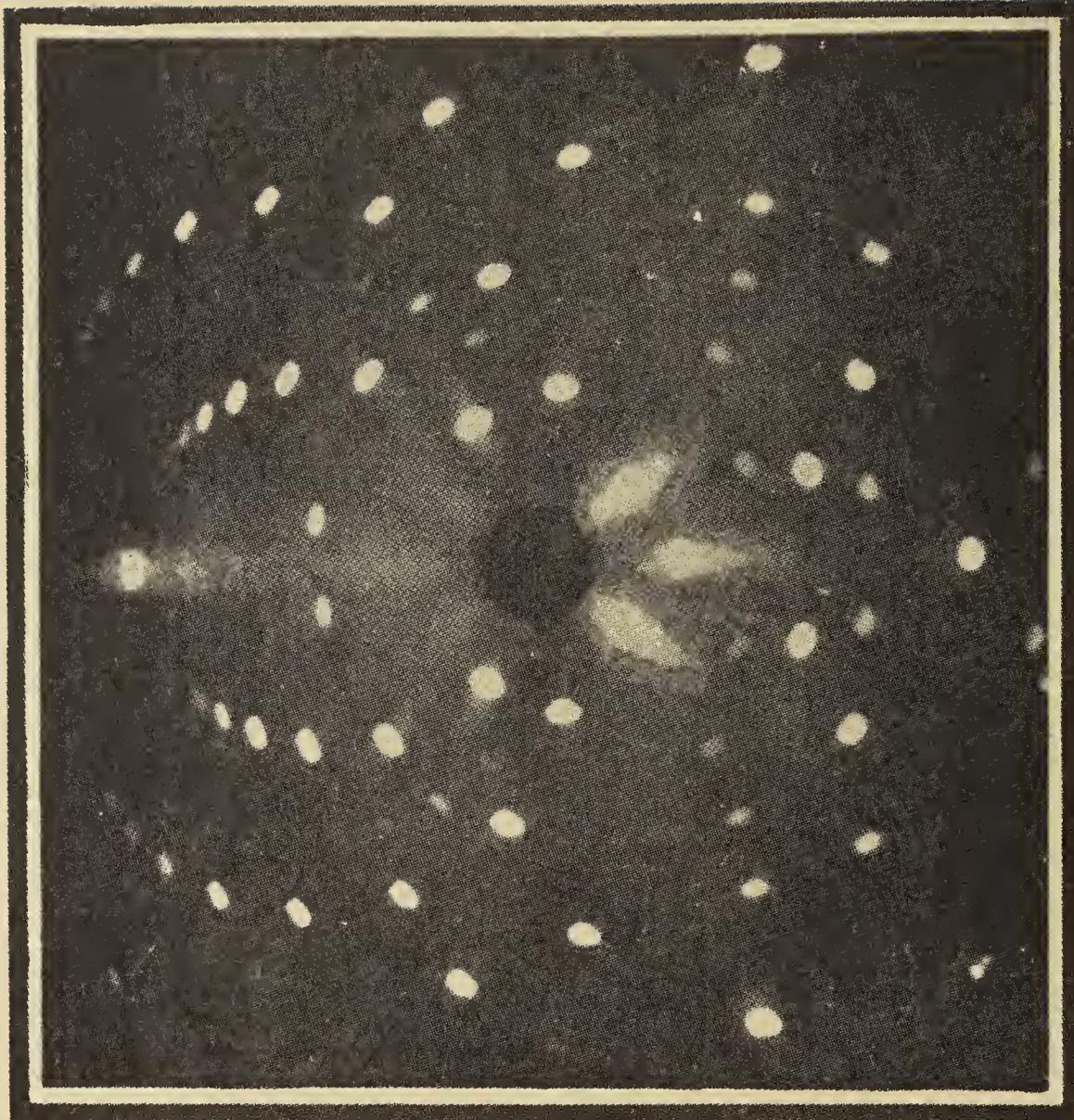
(4)



X-ray beam
inclined
 39° to the
trigonal
axis

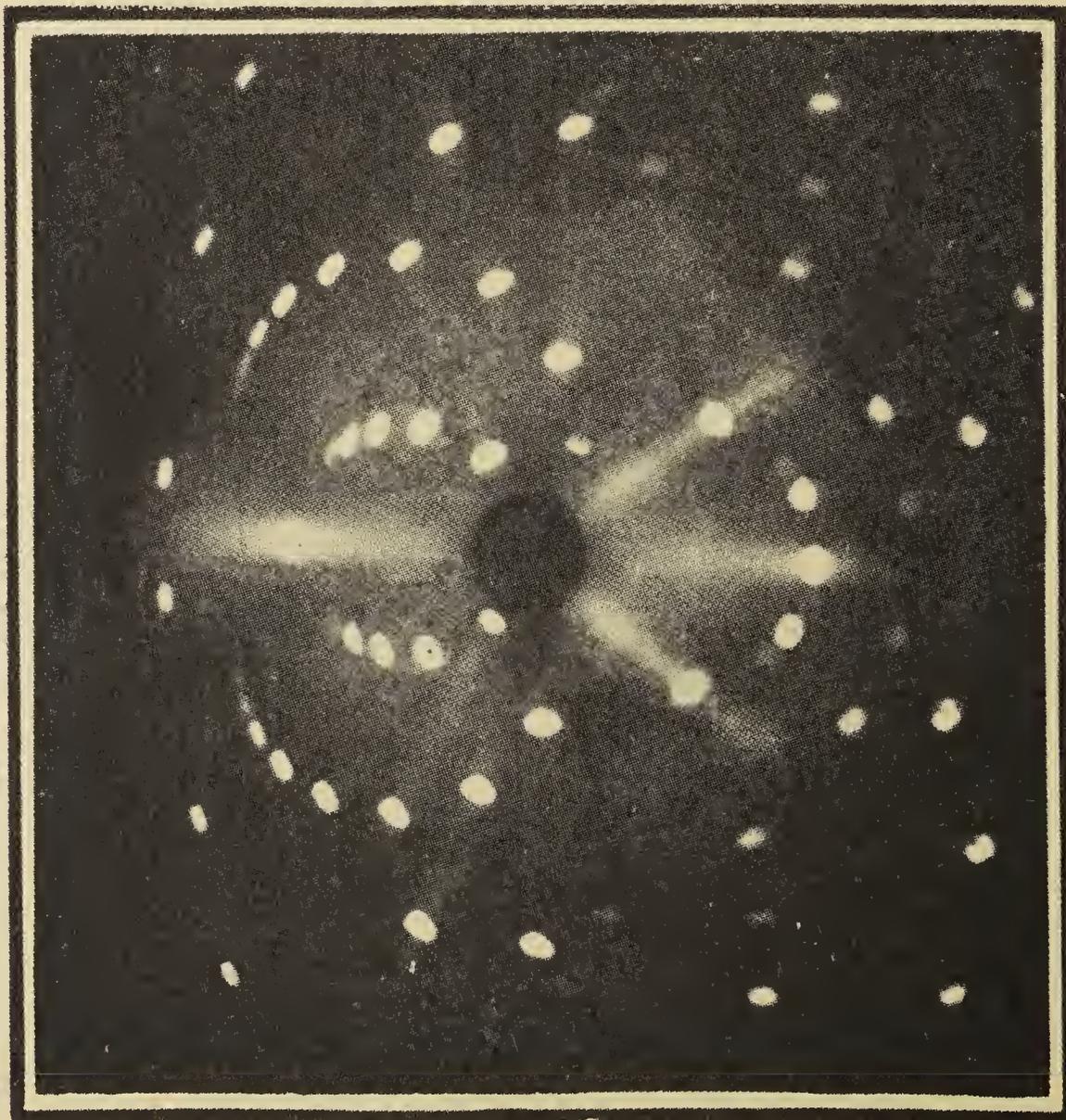
Figures 3 and 4. Laue pattern of sodium nitrate (trigonal axis horizontal).

(5)



X-ray beam
inclined 18°
to $[222]$
planes

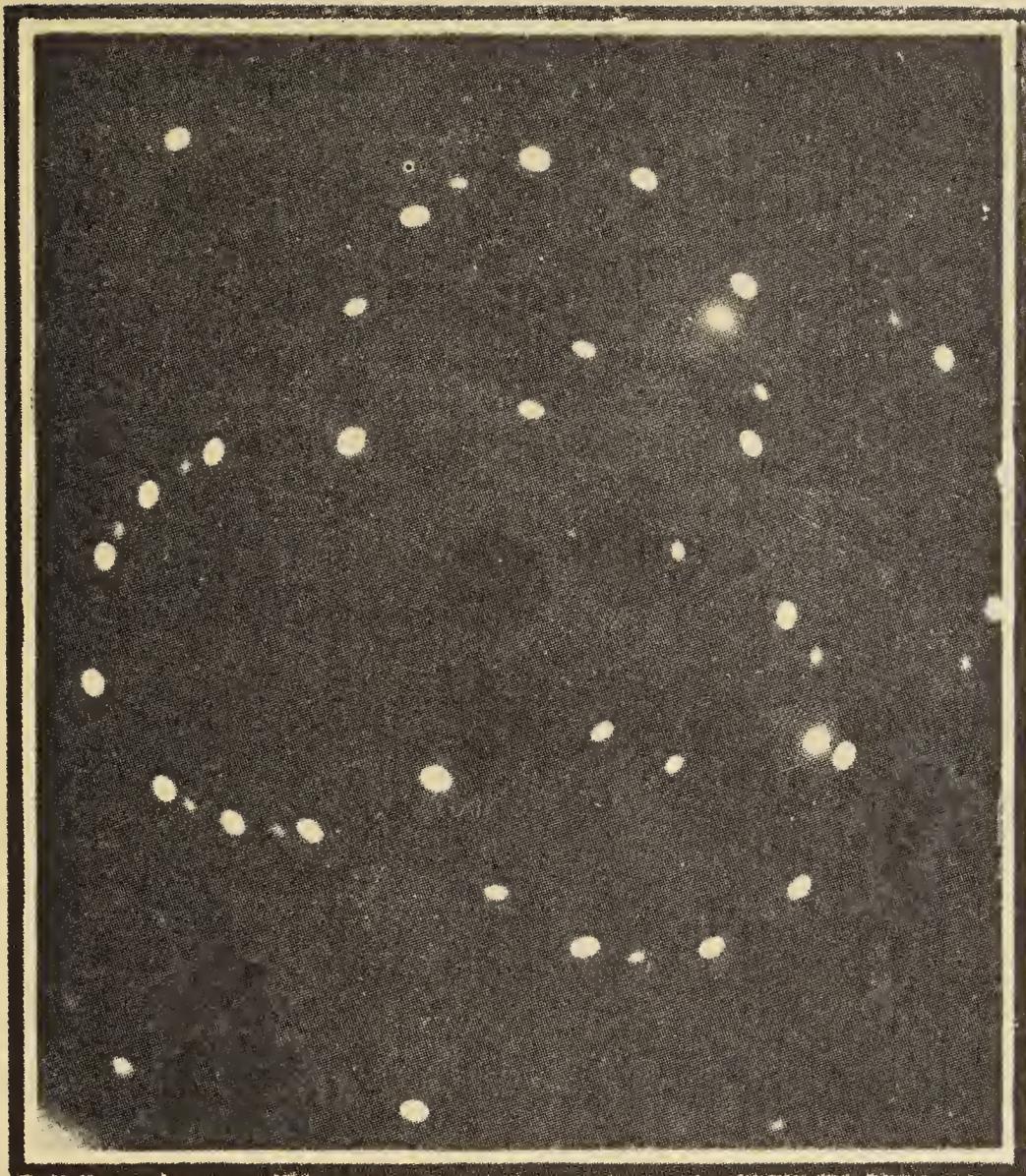
(6)



X-ray beam
inclined 11°
to $[222]$
planes

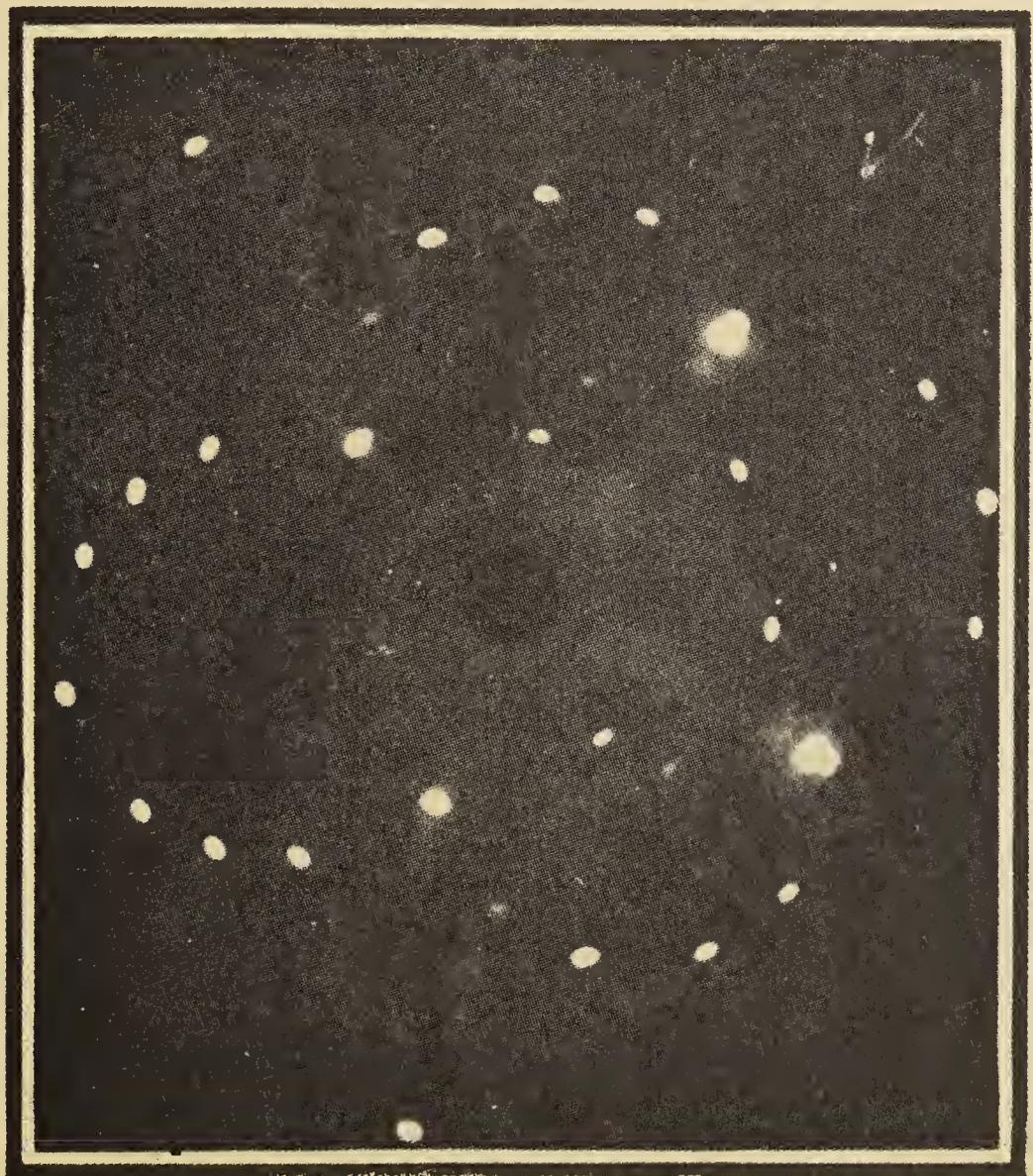
Figures 5 and 6. Laue pattern of sodium nitrate.
Plate III

(7)



25°C

(8)

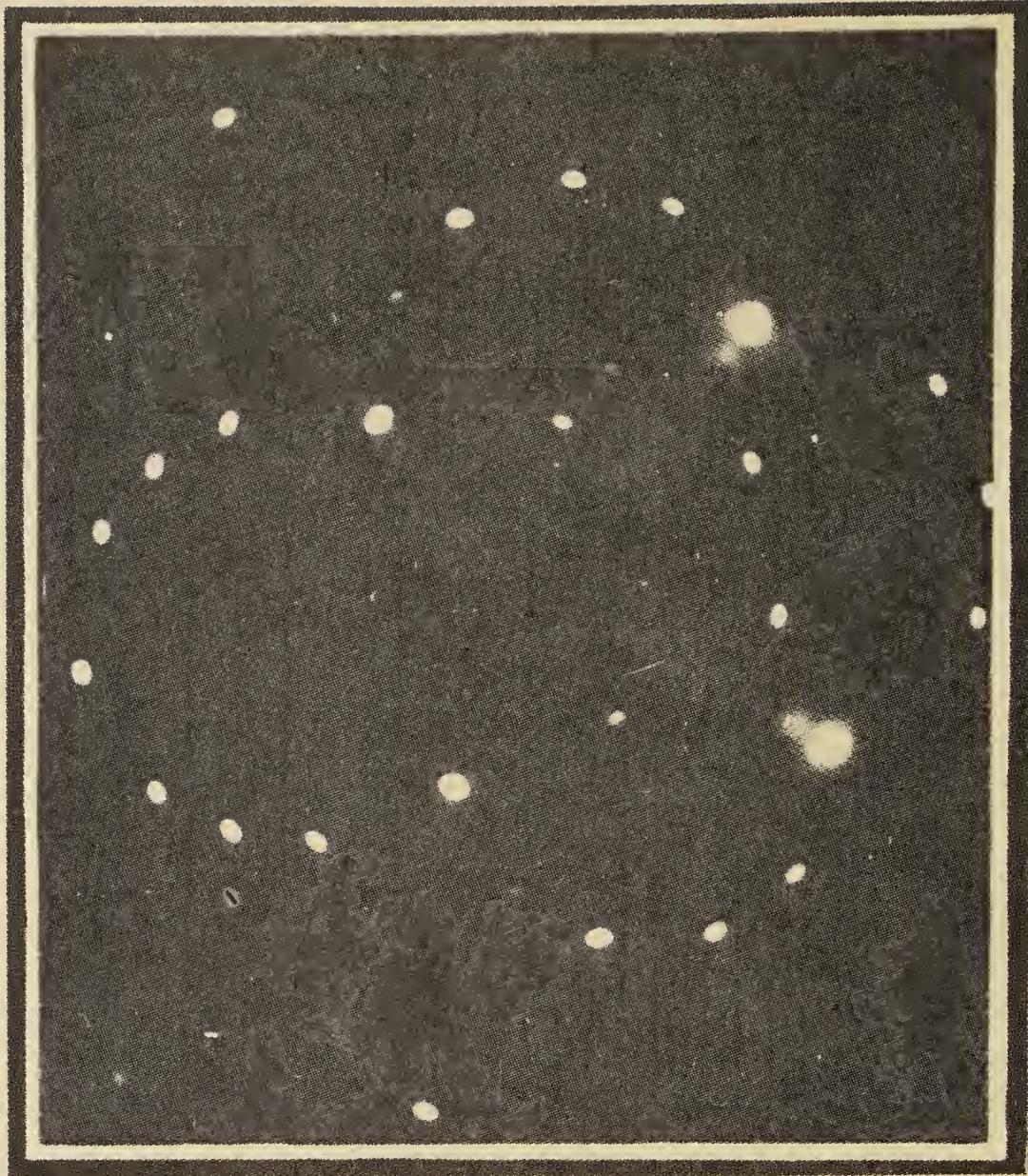


200°C

Figures 7 and 8. Temperature studies with sodium nitrate (X-rays perpendicular to one of the cleavage faces).

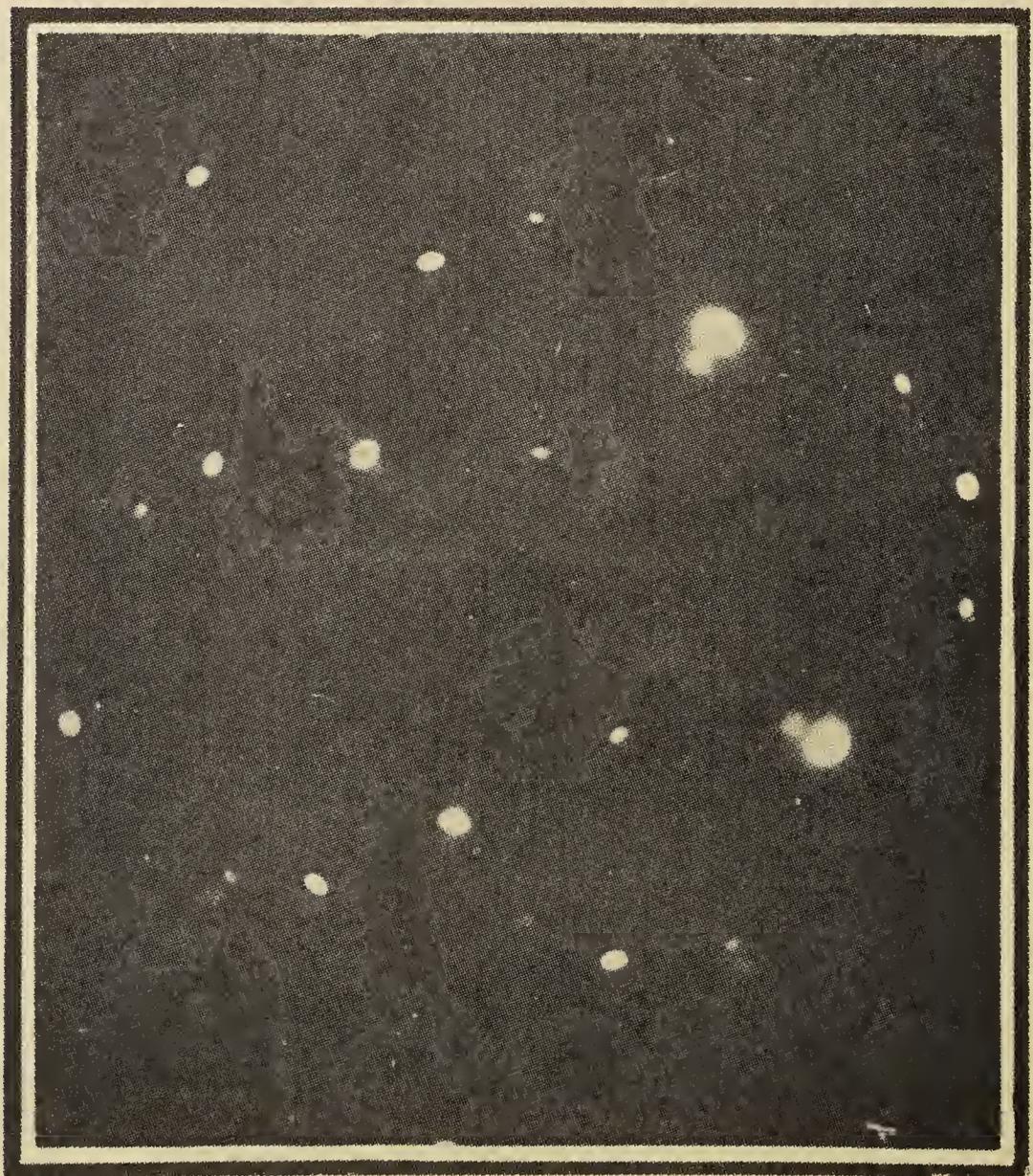
Plate IV

(9)



225° C

(10)



275° C

Figures 9 and 10. Temperature studies with sodium nitrate (X-rays perpendicular to one of the cleavage faces).

Reflection of X-rays with change of frequency— Part IV. Rock-salt

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1. Introduction

The second and third papers of this series (Raman and Nilakantan 1940) described an experimental study of the phenomena observed when X-rays incident on a crystal excite the characteristic vibrations of its lattice structure, resulting in a reflection of the X-rays with altered frequency. The experimental results disclosed remarkable differences between the behaviour of the two crystals studied, namely, diamond and sodium nitrate, in respect of the details of the phenomenon, viz., the geometric law of the modified reflection, the range of incidences over which it may be observed with any particular crystal spacing, the definition which it exhibits at various incidences, the influence of temperature on its intensity, and so forth. These observations indicated the importance of studying the phenomena with a variety of other substances with a view to correlating the results with the crystal structure and infra-red spectrum of the substance. Such a correlation should be possible in the light of the quantum-mechanical theory of X-ray reflection which has been developed and of which the first part has been published in these *Proceedings* (Raman and Nath 1940, I). The present investigation deals with the case of rock-salt, which is of special interest in view of the simplicity of its structure, and has resulted in an advance of our knowledge of the subject in several directions.

2. Lattice structure and lattice vibrations

The structure of rock-salt was one of the earliest to be established by the X-ray method. As is well known, the crystal is built up of sodium and chlorine ions grouped round each other and forming two similar interpenetrating face-centred cubic lattices. The crystal planes which contain equal numbers of sodium and

chlorine ions have the lattice spacing halved and give only the reflections of even orders, while the others in which layers of sodium and chlorine ions alternate exhibit the full lattice spacings and therefore give both odd and even order reflections. In the X-ray reflections of even orders given by both types of spacings, the sodium and chlorine ions co-operate and therefore enhance the intensity, while in the reflections of odd orders given by the undivided spacings, they subtract from each other's effects. The reflections of even and odd orders therefore form two different sequences in one of which the intensity is large and in the other it is small. In both sequences, the intensity falls off as the spacing diminishes (Bragg, James and Bosanquet 1921). Table 1 shows all the reflections observed with rock-salt of which the intensity is 5 per cent or more of the reflections given by the cleavage faces. The figures for the (100), (110) and (111) reflections are taken from the authors quoted, and those for the 210 (2), 211 (2) and 221 (2) reflections are obtained by interpolation from their curve.

Table 1. Spacings and reflection intensities

Halved spacings			Full spacings		
Miller indices	Spacings in A.U.	Reflection intensity	Miller indices	Spacings in A.U.	Reflection intensity
			111(1)	3.250	9
100(2)	2.814	100			
110(2)	1.990	50			
			111(2)	1.625	33
100(4)	1.407	20			
210(2)	1.259	15			
211(2)	1.149	12			
110(4)	0.995	6			
221(2)	0.938	5			
100(6)	0.938	5			

The reflecting power of rock-salt for infra-red radiation shows a large increase over the region of wavelengths from 40μ to 80μ , the curve exhibiting a broad maximum at 52μ . The absorption of infra-red radiation by the crystal is very strong over the whole of this region, but by using a thin layer, it is possible to resolve the transmission curve and observe the principal maximum of absorption at 61μ and feebler subsidiary maxima at 51μ and 41μ (Barnes 1932). It is obvious that an oscillation of the two interpenetrating lattices of sodium and chlorine atoms with respect to each other would give rise to a large electric moment along the direction of movement. Such an oscillation would be strongly active in the infra-red, and the absorption maximum observed at 61μ (164 cm^{-1}) may therefore reasonably be identified with it. Symmetry considerations indicate that

the same oscillation would be inactive in light-scattering. Actually, as has been shown by Fermi and Rasetti (1931), rock-salt exhibits in a very strongly exposed spectrum of light-scattering, a band covering the region of frequency shift from 160 cm^{-1} to 365 cm^{-1} with a series of intensity maxima clearly visible within this range. This has been explained by Fermi and Rasetti as a second-order effect. The lower frequency limit of the band, it will be noticed, is about the same as the characteristic infra-red absorption frequency, and the upper limit approximately the octave of it. In view of these facts, it appears justifiable to conclude that the principal optical frequency of the rock-salt structure is 164 cm^{-1} and that this frequency corresponds to a movement of the two interpenetrating lattices with respect to each other.

Owing to the cubic symmetry of the crystal, the oscillation referred to above would be triply degenerate, that is, may take place in any arbitrary direction with the same frequency. It is also evident that the oscillation would influence the structure amplitude of all the crystal spacings except such as happen to be actually parallel to it. Considering the lattice planes containing equal numbers of sodium and chlorine ions, the average electron density exactly midway between such planes would be neither increased or decreased by an oscillation in which adjacent sodium and chlorine ions alternately approach and recede from each other. Nearer the planes, however, the electron density would be increased in one half of the oscillation and decreased in the other half, or *vice versa*. The wavelength of the oscillation of electron density would therefore be the same as the distance between such planes, and its time-period identical with that of the oscillation of the lattices. In the case of the planes which contain only sodium or chlorine ions alternately, the electron density midway between such planes is increased in one half of the oscillation and decreased in the other half, or *vice versa*. Here again, therefore, the wavelength of the oscillation of electron density is the same as the distance from one plane of atoms to the next of the same kind. In other words, the dynamic stratifications of electron density have their spacings halved or not halved, in the same way as the corresponding static periodicities.

The considerations set out above indicate that table 1 which is a list of the spacings in rock-salt which give intense unmodified reflections would equally well represent a list of the spacings giving strong modified reflections as the result of the oscillations of the lattice structure. All the lattice planes except (111) should give the even order reflections only, and we may further expect the intensity of these reflections to fall off in a regular sequence with the diminution of the crystal spacings in much the same way as for the unmodified reflections. The case of the (111) planes, however, requires special consideration. The static structure amplitude of these planes is greater for the second order than for the first, the intensities of these reflections being in the ratio 33:9. The characteristic vibration of the crystal structure would however influence the structure amplitude more for the first order than for the second order, the movements of the two interpenetrating lattices being in opposite directions. Accordingly, the intensity of the modified

reflections of the first and second orders from the (111) planes should not exhibit such a large disparity as the unmodified reflections of these orders.

3. Geometry of modified reflection

The geometric relations entering in the modified reflection of X-rays have been discussed in detail on the basis of the quantum theory by Raman and Nath (1940) in a recent paper in these *Proceedings*. The results briefly stated are: the modified reflection appears in the plane of incidence of the X-ray beam on the crystal spacing under consideration; the glancing angles of incidence and reflection θ and ϕ respectively are, in general, not equal to each other, but satisfy the relation

$$2d \sin \frac{1}{2}(\theta + \phi) = n\lambda; \quad (1)$$

the intensity of the reflection is greatest when $\theta = \phi$ and falls off when θ and ϕ diverge from each other, at first very rapidly, and later more slowly. These three results enable us readily to determine the general features of the modified reflections appearing in a Laue pattern for any stated orientation of the crystal.

Equation (1) indicates that *the angular separation between the incident beam and the modified reflection from any particular spacing is independent of the setting of the crystal*. Round the centre of the pattern (viz., the point at which the incident beam meets the photographic plate), we draw a series of circles on the plate corresponding to this angular separation for each of the crystal spacings capable of giving modified reflections of sufficient intensity to be observed. It will be seen from equation (1) that the position of these circles on the plate would coincide with the rings in the powder-pattern of the crystal for the same plate distance. From the centre of the pattern, we then draw a set of radial lines on the plate such that each such line and the incident X-ray together define the plane of incidence of the latter on the particular crystal spacing under consideration. The points at which the circles and the radial lines intersect give the positions of the modified reflections. If the wave-length of the X-ray is changed, the powder-diagram circles would expand or contract, and the modified reflections would therefore move in or out along the radial lines. The modified reflection of the white radiation present in the incident pencil would therefore appear as a radial streak on the same line as the spots due to the monochromatic rays.

Since the angles θ and ϕ may have any values satisfying equation (1), it is not necessary for recording a modified reflection that the particular crystal plane should be in such an orientation as to give a Laue reflection observable on the plate. We may, for instance, have $\theta = 0$, in other words, the incident ray grazes the crystal plane, in which case the Laue reflection would be unobservable but the modified reflection would appear at an angle ϕ with the incident beam given by the relation

$$2d \sin \frac{1}{2}\phi = n\lambda. \quad (1a)$$

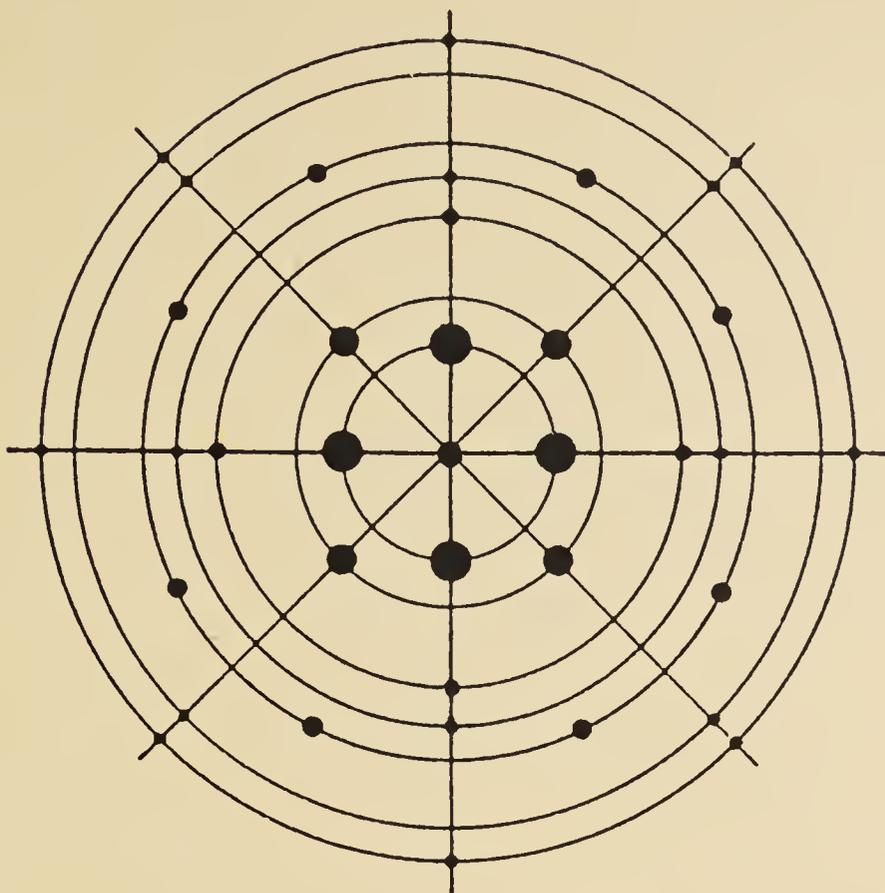


Figure 1. Pattern of modified reflections: direction of incidence $[100]$.

It may be remarked also that θ and ϕ need not be positive. One of them may be positive and the other negative, and the integer n which gives the order of the reflection may be either positive or negative. The range of admissible values of θ and ϕ and the permissible values of n are, however, limited by considerations of intensity. If θ and ϕ differ too widely, or if n be too large, the modified reflection may be unobservable. Figures 1 and 2 represent the modified reflection patterns drawn in this way for the cases in which the incident X-ray beam traverses the $[100]$ and $[110]$ directions respectively within the crystal. The circles drawn in these figures are the Debye-Scherrer rings for the crystal spacings listed in table 1. Since the 441 and 600 spacings are identical, there are only nine rings to be considered. In figure 1, the 111 and 222 circles have been omitted, as the value of θ for these spacings would be too large for the corresponding modified reflection to be of observable intensity. They however appear in figure 2. In both of these cases, the incident X-ray grazes some of the planes giving the strongest modified reflections. For instance, a beam along $[100]$ grazes the following planes: (001), (010), (011) and (0 $\bar{1}$ 1). A beam along $[110]$ grazes the following planes: (001), ($\bar{1}$ 10), ($\bar{1}$ 11) and (1 $\bar{1}$ 1). Accordingly, in these cases, the reflections by these planes appear in the directions given by the formula (1a) and form an important features of the observed patterns. Other reflections can also appear on the pattern if the orientation of the planes in question is not too remote from that necessary for a Bragg reflection. These have also been drawn in the figures.

It is interesting to consider in what way the pattern represented in figure 1, would be altered if the orientation of the crystal is altered, step by step, by rotating

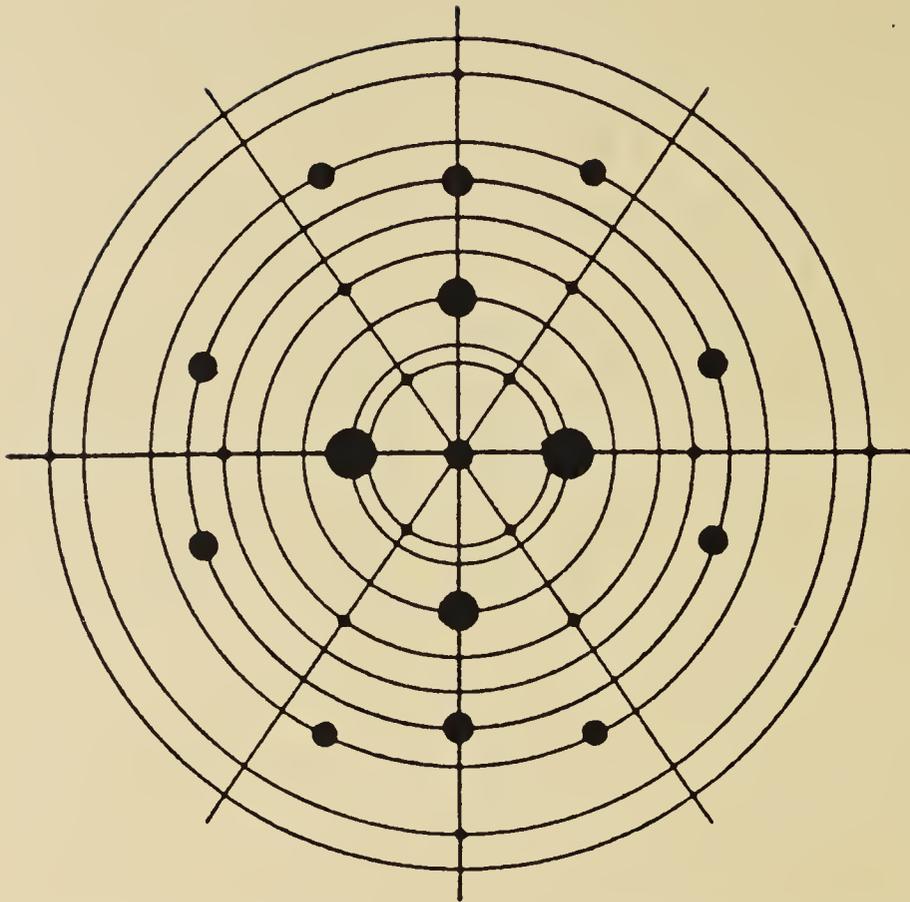


Figure 2. Pattern of modified reflections: direction of incidence $[110]$.

it about a suitable axis. The X-ray beam has initially the direction $[100]$ within the crystal, and the latter is then rotated about a perpendicular direction, say $[010]$, a few degrees at a time. By virtue of formula (1), the modified reflections would in such a case continue to lie on their respective circles. It is obvious, however, that with the exception of the reflections appearing in the plane containing the axis of rotation, the modified reflections must move along the circles which are their loci in order that they may remain in the respective planes of incidence. To find their position rigorously, it would be necessary, at each setting of the crystal to find anew the planes of incidence and redraw the radial lines in the diagram the intersection of which with the circles of the powder-diagram gives the modified reflections. The trouble of doing this may, however, be avoided and the positions located with fair accuracy by a simple device, namely by finding the layer lines on which appear the Bragg reflections when the crystal is rotated or oscillated about the specified axis. It is evident that the points at which these layer lines intersect the powder-diagram circles represent the position of the modified reflections *rigorously* for the particular orientation of the crystal at which they coincide with the corresponding Bragg reflections, and therefore *approximately* also for a considerable range of orientations on either side of that position. In figure 3, the layer lines have been drawn for the case mentioned above, and the positions of the modified reflections marked therein. On comparing the same with figure 1, it will be seen that the displacements from their positions in the normal setting of the crystal are not large.

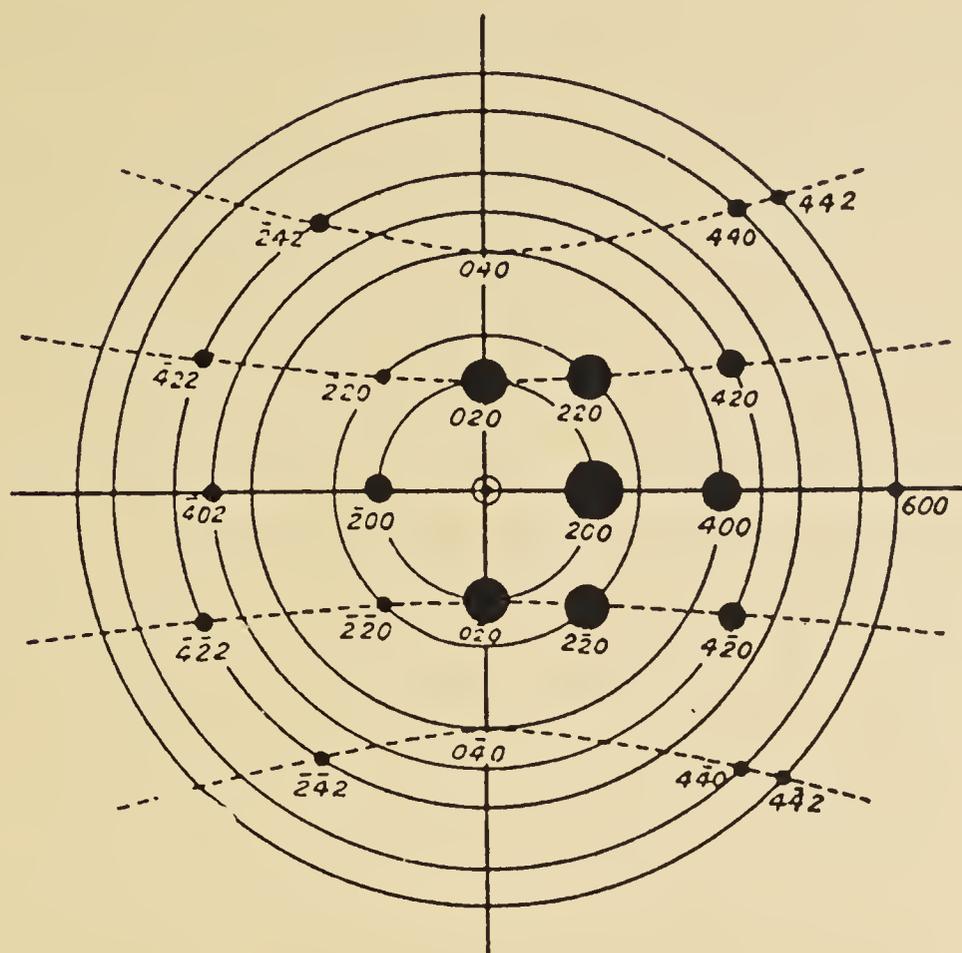


Figure 3. Pattern of modified reflections with crystal tilted about $[010]$ axis.

4. Experimental results

Plates I, II and III reproduce a series of 12 Laue photographs (figures 4 to 15) obtained with a crystal of rock-salt and the unfiltered radiation from a molybdenum target, the distance from crystal to photographic film being 4.9 cms in the whole series. In obtaining figure 4, the crystal was set with the X-ray beam normal to a cube-face, in other words parallel to an axis of four-fold symmetry, and the pattern accordingly shows the same type of symmetry. In obtaining the remaining seven photographs of the series figures 5 to 11, the setting of the crystal was altered a few degrees at a time, being turned round a vertical axis of four-fold symmetry in the crystal. The patterns accordingly exhibit two-fold symmetry about a horizontal axis. The inclination of the X-ray beam to the four-fold axis of symmetry increased from 0° in figure 4 to $17^\circ 46'$ in figure 11. Figures 12 to 15 in plate III reproduce another series of Laue photographs obtained by the same procedure but at larger angular intervals for the setting of the crystal and covering a greater range of incidences. To permit of this being done, the photographic film was displaced sideways so that it exhibits only one half of the Laue pattern. The inclination of the X-ray beam to the four-fold axis of symmetry was 0° in figure 12 and $25^\circ 21'$ in figure 15. Plate IV reproduces two Laue photographs (figures 16 and 17) obtained with the unfiltered X-radiation from molybdenum and copper targets respectively, the rock-salt crystal being set so

that the X-ray pencil was parallel to a diagonal axis of symmetry, in other words inclined at 45° to the cube faces.

A careful study of the Laue photographs reproduced in the plates brings out clearly the laws of the modified reflection of X-rays. The series of figures 4 to 15 in the plates should be compared with figure 1 and figure 3 in the text above in which the theoretical positions of the modified reflections have been indicated. Figures 16 and 17 in the plate may also be compared with figure 2 in the text which refers to the same orientation of the crystal. It will be seen that there is a satisfactory agreement in each case between the theory and the experimental results. The most striking features brought out by the photographs are (1) the invariability of the angular separation between the incident beam and the modified reflections and (2) the remarkable resemblance between the pattern of modified reflections for an oblique setting of the crystal with the layer-line diagram of an oscillating or rotating crystal. This resemblance is clearly the consequence of the mechanism by which the modified reflections are brought into existence, namely the rotation of the dynamic stratifications of electron density with respect to the crystal spacings by the phase-waves of the lattice vibration. The rotation is of such magnitude that the angle $(\theta + \phi)$ between the incident pencil and the modified reflection by any particular plane remains invariant, though the crystal setting is altered. In other words, the modified reflection appears at the same angular separation from the primary beam as the Bragg reflection for a different setting of the crystal.

5. Intensity relations

We shall now proceed to consider in detail the remarkable changes which occur in the *intensity* of the modified reflections as the setting of the crystal is altered. These form an impressive feature in the photographs.

The most intense reflections are those given by the (100) planes, as is to be expected. These are observed over a wide range of incidences in the second, fourth and sixth orders, but in decreasing order of intensity. The second order may be positive or negative, the reflection in the latter case appearing on the side of the plane opposite to that on which the X-ray beam is incident, which is rather a noteworthy phenomenon. Modified reflections of several different orders may be simultaneously observed, and in such cases, the relative intensity of the different orders depends on the setting of the crystal. For instance, in figures 14 and 15, the second, fourth and sixth order reflections by the (100) planes may all be observed, but the fourth order is the most intense in figure 14 and the sixth order in figure 15. The intensity of a reflection of any particular order is greatest when θ and ϕ are nearly equal, that is when the modified reflection appears in the vicinity of an ordinary or Bragg reflection of the same order from the planes under consideration. The intensity falls off when θ and ϕ diverge from each other in either direction. This fall is very rapid when θ is nearly equal to ϕ , as is evident

from the photographs and strikingly illustrated by the fact (see for instance figure 9) that the K_β reflection may actually be stronger than the K_α reflection when it is nearer the Laue spot due to the same spacing. The fall of intensity however, becomes relatively slow when θ and ϕ differ greatly, and this fact enables the modified reflections to be observed over a wide range of incidences.

The (110) planes also give intense modified reflections, which may be observed in the second order, positive as well as negative and, though rather weakly, also in the fourth order (see figure 15). That these reflections are definitely weaker than the corresponding (100) reflections, may be seen for instance from figure 7, in which the second order (negative) reflections from the (110) planes have almost vanished, while those from the (100) are still quite strong. In some settings of the crystal, the (110) reflections may appear stronger than the corresponding (100) reflections, e.g., in figures 14 and 15 where the 220 spots are stronger than the 200 spots, but this is merely due to the great disparity in the relative values of θ and ϕ for the two reflections.

Next in order of intensity are the 420 modified reflections, i.e., those by the (210) planes in the second order. They may be seen above and below the 400 modified reflections and on the same layer line as the 020 and 220 modified reflections (figures 10, 11, 13, 14 and 15) and may be readily compared in intensity with them. It will be noticed that the (420) spots though less intense than the 020 and 220 spots are comparable in intensity with the 400 spots and in some photographs actually brighter than them (see for instance figure 15). These observations indicate that the modified reflections by the crystal planes appearing in the first column of table 1 follow the same order of intensity as the unmodified reflections by those planes. The figures given in table 1 further suggest that the 422 modified reflections should be weaker than the 420 and 400 modified reflections. That this is actually the case may be seen from figure 11 in which these reflections are seen in comparable circumstances (the 420 and 400 spots in the right half of the picture, and the 422 spots in the left half). See also figures 6, 8, 9 and 11. From table 1, we may also expect that the (221) planes should give modified reflections (in the second order) of comparable intensity with the fourth order reflections from the (110) planes and the sixth order reflections from the (100) planes. The 442 reflections may be seen clearly in figure 5 and their intensity is about the same as the 110 (4) and 100 (6) reflections seen in figure 15 in comparable circumstances.

6. Verification of the modified Bragg formula

In the theoretical paper by Raman and Nath quoted above, two alternative formulae have been deduced, namely

$$2d \sin \frac{1}{2}(\theta + \phi) = n\lambda, \quad (1)$$

$$d \sin (\theta + \phi) = n\lambda \cos \phi, \quad (2)$$

which connect the glancing angles of incidence and reflection θ and ϕ respectively with the crystal spacing d , the order of reflection n and the X-ray wavelength λ . It was indicated that the considerations on which formula (1) was derived were probably valid for the great majority of crystals. In the preceding discussion, formula (1) has been assumed to be correct, but it is evidently of importance that the experimental data should be compared with both of the formulae as a test of the theoretical considerations on which they were respectively based. The results given by the two formulae differ to a greater extent the more widely θ and ϕ diverge from each other. The formulae however become identical when $\theta = \phi$. Further, if the angles θ and ϕ are small,

$$2 \sin \frac{1}{2}(\theta + \phi) \approx \sin(\theta + \phi) \text{ and } \cos \phi \approx 1,$$

and hence in these circumstances the two formulae cease to be experimentally indistinguishable. Accordingly for a discrimination between them to be possible, it should be based on those cases when θ and ϕ differ considerably, and ϕ is as large as possible.

We give below in a series of tables, the data measured from the photographs for the various orders of reflections by the spacings listed in the first column of table 1.

The figures appearing in the last two columns of tables 2, 3, 4, 5, 6, 7, 8 and 9 all show in an unmistakable manner that the symmetric formula (1) and *not* the

Table 2. 200 Reflections: crystal spacing = 2.814 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
+100(2)	0.708	0°	14°19'	14°19'	2.84	2.77
		2°17'	11°55'	14°12'	2.86	2.82
		3°33'	10°46'	14°19'	2.84	2.81
		4°4'	10°21'	14°25'	2.82	2.80
		9°40'	4°45'	14°25'	2.82	2.83
		11°36'	2°43'	14°19'	2.84	2.86
		14°47'	-0°35'	14°12'	2.86	2.89
		17°46'	-3°34'	14°12'	2.86	2.88
		25°21'	-11°9'	14°12'	2.86	2.83
+100(2)	0.625	0°	12°39'	12°39'	2.83	2.79
		4°4'	8°35'	12°39'	2.83	2.82
		9°40'	2°46'	12°26'	2.89	2.90
		11°36'	1°3'	12°39'	2.83	2.85
-100(2)	0.708	0°	-14°12'	-14°12'	2.86	2.80
		2°17'	-16°36'	-14°19'	2.84	2.74
		3.33'	-17°52'	-14°19'	2.84	2.72
		4°4'	-18°16'	-14°12'	2.86	2.74
		9°40'	-23°59'	-14°19'	2.84	2.62

Table 3. 220 Reflections: crystal spacing = 1.990 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
+(110)(2)	0.708	0°	20°10'	20°10'	2.02	1.93
		4°21'	15°55'	20°16'	2.01	1.97
		6°53'	13°31'	20°24'	2.00	1.98
		7°58'	12°26'	20°24'	2.00	1.98
		12°20'	7°50'	20°10'	2.02	2.03
+(110)(2)	0.625	6°53'	10°53'	17°46'	2.02	2.01
		10°20'	7°32'	17°52'	2.01	2.02
		12°20'	5°20'	17°40'	2.04	2.05
-(110)(2)	0.708	0°	-20°10'	-20°10'	2.02	1.93
		1°39'	-21°49'	-20°10'	2.02	1.91
		1°51'	-22°1'	-20°10'	2.02	1.90
		2°14'	-21°53'	-19°39'	2.07	1.95

Table 4. 400 Reflections: crystal spacing = 2.814 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(100)(4)	0.708	9°40'	19°18'	28°58'	2.83	2.76
		11°36'	17°26'	29°2'	2.82	2.78
		17°46'	11°22'	29°8'	2.82	2.85
		19°21'	9°57'	29°18'	2.80	2.85
		25°21'	3°57'	29°18'	2.80	2.89
(100)(4)	0.625	9°40'	15°58'	25°38'	2.82	2.78
		11°36'	14°8'	25°44'	2.81	2.79
		14°47'	10°57'	25°44'	2.81	2.83
		17°46'	7°58'	25°44'	2.81	2.85

asymmetric formula (2) gives results in agreement with experiment in the case of rock-salt. The differences between the actual crystal spacings and those calculated from the asymmetric formula are systematic and in the expected direction: they increase when θ and ϕ diverge from each other, being positive when θ is greater than ϕ and negative when θ is less than ϕ . The differences become great when ϕ is numerically large, just as we should expect. The errors in measurements of the angles of θ and ϕ are relatively the greatest in the case of the 200 reflections, both because the absolute values of θ and ϕ are then smallest, and also because the spots being intense, are heavily overexposed and therefore

Table 5. 240 and 420 Reflections: crystal spacing = 1.259 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(120)(2) and (210)(2)	0.708	13°3'	19°27'	32°30'	1.27	1.24
		13°17'	19°13'	32°30'	1.27	1.24
		14°53'	17°37'	32°30'	1.27	1.26
		15°24'	17°14'	32°38'	1.26	1.25
		15°32'	17°2'	32°34'	1.26	1.26
		16°59'	15°35'	32°34'	1.26	1.27
	0.625	13°3'	15°27'	28°30'	1.27	1.26
		13°17'	15°19'	28°36'	1.27	1.26
		14°53'	13°59'	28°52'	1.25	1.26
		15°24'	13°20'	28°44'	1.26	1.26
		15°32'	12°58'	28°30'	1.27	1.28
		16°59'	11°53'	28°52'	1.25	1.27

Table 6. 242 and 422 Reflections: crystal spacing = 1.149 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacings calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(121)(2) and (211)(2)	0.708	15°6'	20°36'	35°42'	1.15	1.13
		15°32'	20°20'	35°52'	1.15	1.13
		16°29'	19°27'	35°56'	1.15	1.14
		16°59'	18°57'	35°56'	1.15	1.14
		18°32'	17°24'	35°56'	1.15	1.15
		20°29'	15°27'	35°56'	1.15	1.16
	0.625	20°35'	15°21'	35°56'	1.15	1.16
		15°6'	16°24'	31°30'	1.15	1.15
		15°32'	16°4'	31°36'	1.15	1.15
		16°29'	16°11'	31°40'	1.15	1.14
		16°59'	14°53'	31°52'	1.14	1.15
		18°32'	13°8'	31°40'	1.15	1.16

subject to photographic broadening. It is therefore not surprising that the agreement between the actual crystal spacings and those calculated from the symmetric formula and shown in the penultimate column of table 2 is not as excellent as it is in the case of the reflections listed in tables 3 to 9. Even so, the

Table 7. 440 Reflections: crystal spacing = 1.990 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(110)(4)	0.708	17°29'	24°19'	41°48'	1.99	1.94
	0.625	17°29'	18°49'	36°18'	2.01	2.00

Table 8. 442 Reflections: crystal spacing = 0.938 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(221)(2)	0.708	20°48'	23°36'	44°24'	0.937	0.927
		21°27'	22°47'	44°14'	0.940	0.935

Table 9. 600 Reflections: crystal spacing = 2.814 A.U.

Crystal planes and order of reflection	X-ray wavelength A.U.	Glancing angle of incidence θ	Glancing angle of reflection ϕ	$\theta + \phi$	Spacing calculated from	
					Formula (1) A.U.	Formula (2) A.U.
(100)(6)	0.708	19°21'	24°45'	44°6'	2.83	2.74
		25°21'	19°3'	44°24'	2.81	2.87

failure of the asymmetric formula for the 200 reflections is as evident as in the other cases.

7. Significance of the results

The asymmetric formula (2) referred to above may be written in the form

$$d(\sin \theta + \cos \theta \tan \phi) = n\lambda. \quad (2')$$

A formula of identically the same form as (2') appears as equation (12) of a theoretical paper by Faxen (1923) in which ϕ now denotes the direction of maximum intensity in the diffuse thermal scattering of monochromatic X-rays by a cubic crystal. Faxen's theory has been recently revived and developed by Zachariasen

(1940) in an attempt to explain the radial streaks in Laue patterns observed by many workers as well as the more recent experimental results obtained in this connection by Wadlund (1938), Preston (1939) and of Siegel and Zachariasen (1940). As we have seen above, the formula (2') fails to represent the actual position of the modified reflections observed with rock-salt when the incidences are varied over a sufficient range of angles to make a real test of its validity. The experimental results thus clearly indicate that the Faxen-Zachariasen theory is inadequate to explain the phenomena under consideration in the present series of papers. Further, the success of the modified Bragg formula (1) in giving correctly the position of the spots as observed in the present investigation over a wide range of incidences indicates clearly that we are dealing here with a distinctive phenomenon which is in the nature of a specular reflection of the X-rays, and not a diffuse scattering.

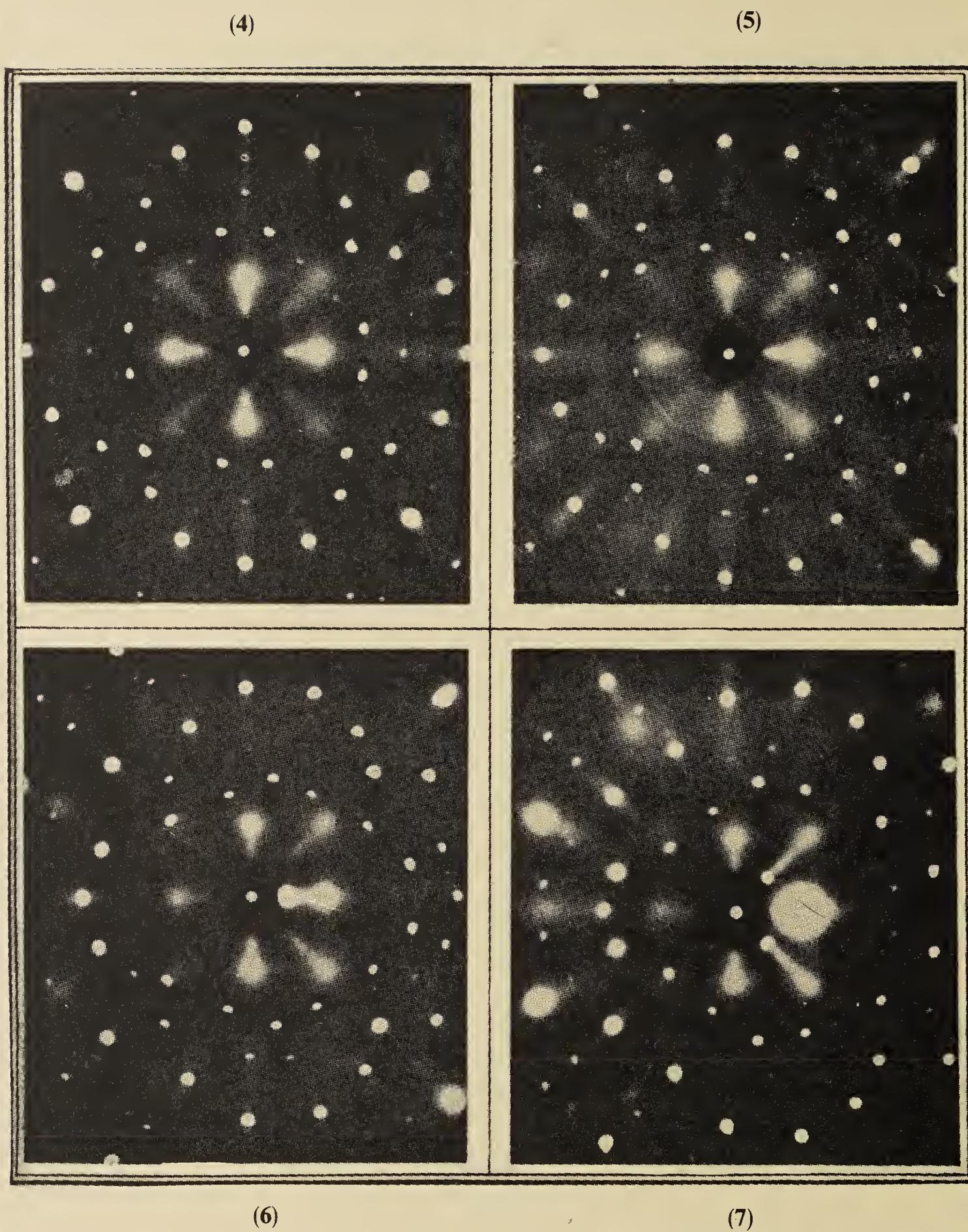
It will be noticed that the modified reflections given by rock-salt are much better defined than those obtained with sodium nitrate, especially when the angles of incidence and reflections differ greatly. This is not surprising when it is remembered that the melting point of rock-salt is 804°C as against 308°C for sodium nitrate, and that the characteristic frequencies of the latter substance (at any rate some of them) are much lower than that of rock-salt. The disturbing effect of thermal agitation on the modified reflections should therefore be much more serious with sodium nitrate than with rock-salt. The theoretical derivation of the symmetric formula makes it clear that the reflections given by that formula should appear in sharply defined directions, and any lack of definition must therefore be due to disturbing causes such as thermal agitation or the mosaic structure of the crystal. The question here raised can be resolved by experiments with the substance at low temperatures. Such experiments have been taken in hand.

8. Summary

The paper presents an experimental study and theoretical discussion of the modified reflection of X-rays in rock-salt. It is shown that the oscillation of the interpenetrating lattices of sodium and chlorine ions would vary the structure amplitudes of the crystal in such a way that the halved spacings which give strong unmodified reflections would also give strong modified reflections in the same order of relative intensity. This is supported by the experimental results. A geometrical construction is given for deriving the modified reflection patterns in various cases and it is shown that for an oblique setting of the crystal, there is a remarkable similarity between the patterns and the layer-line diagram of the Bragg reflections by an oscillating crystal. The modified Bragg law $2d \sin \frac{1}{2}(\theta + \phi) = n\lambda$ is in very satisfactory agreement with the experimental result.

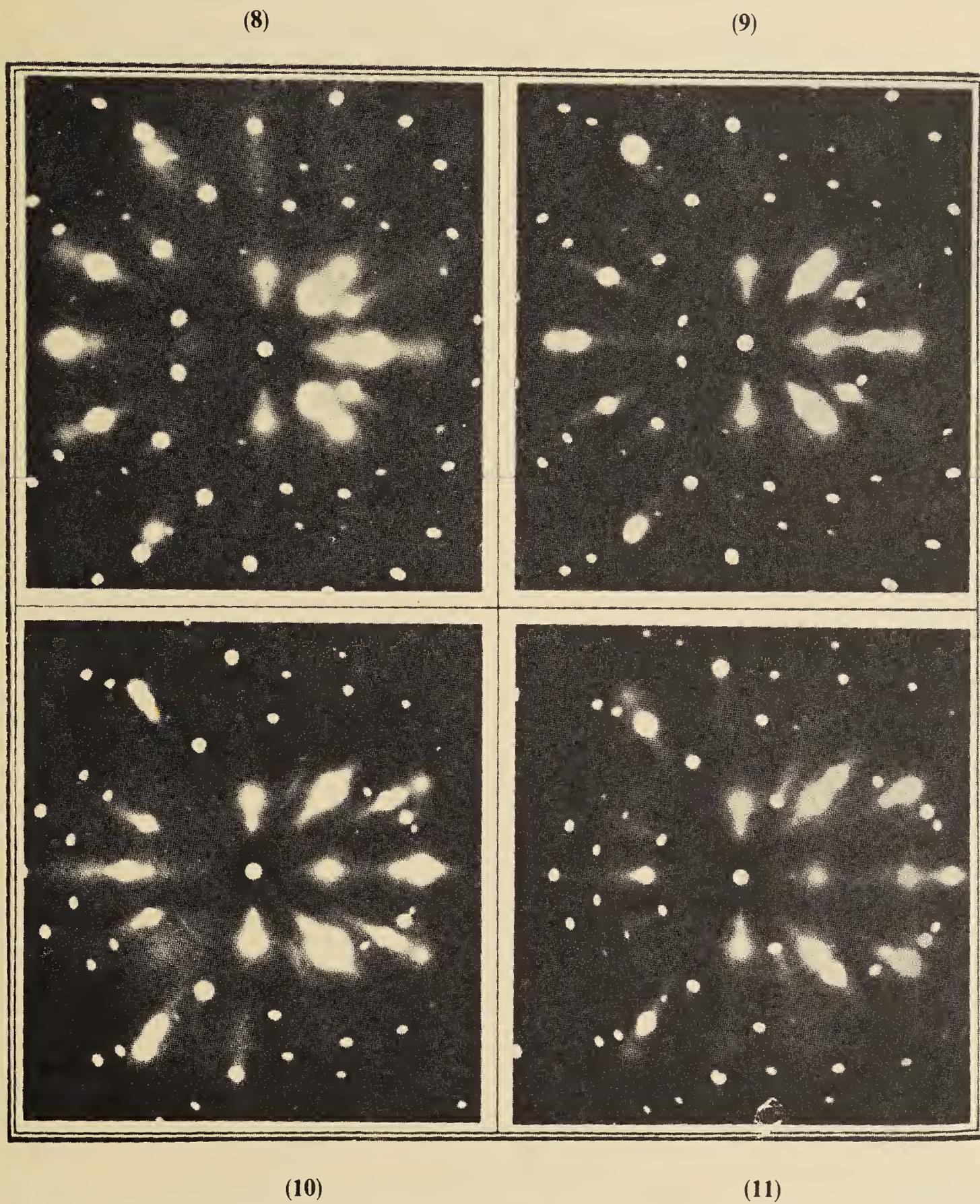
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Figures 4-7. Laue photographs with rock-salt showing modified reflections.

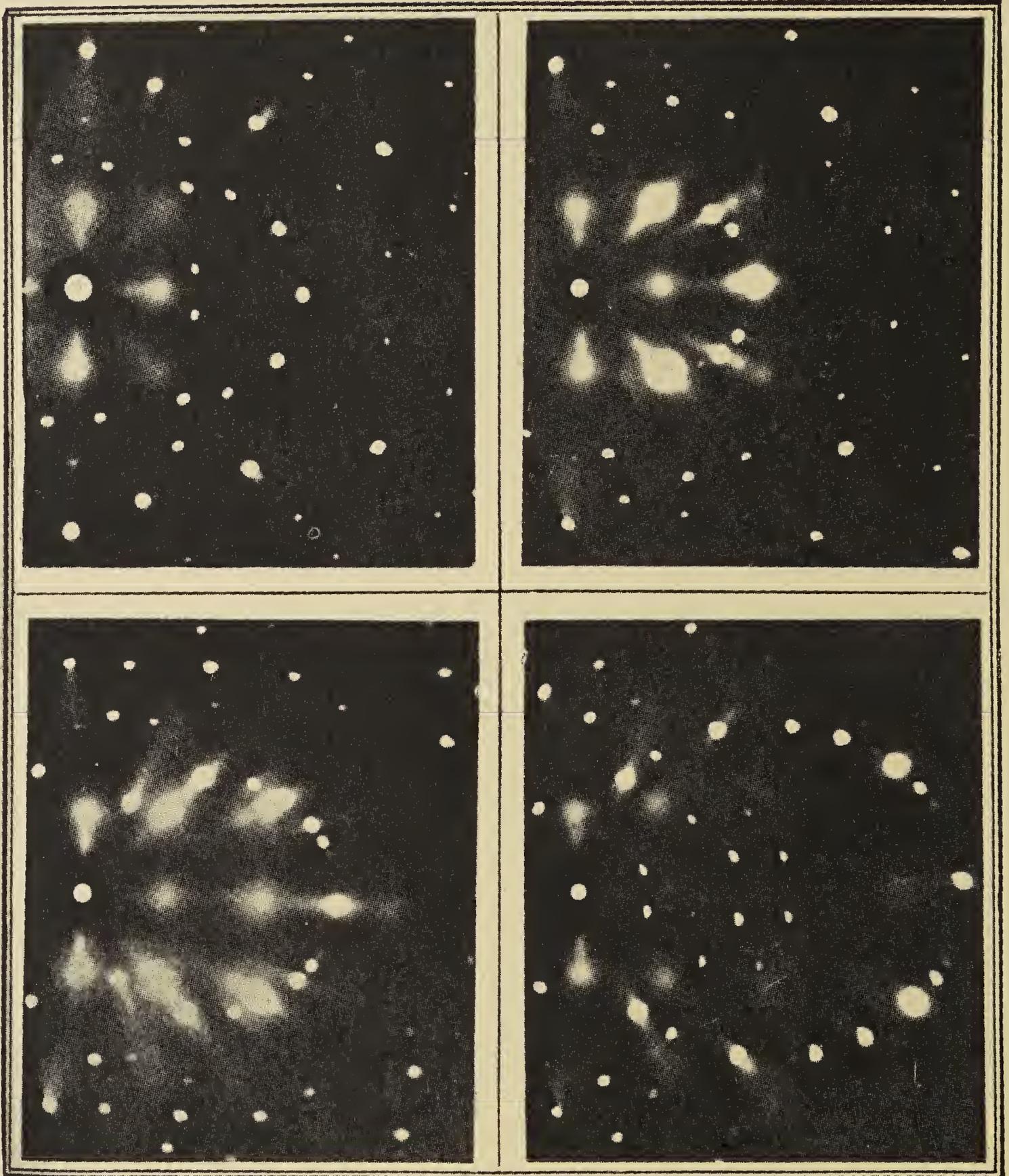
Plate I



Figures 8-11. Laue photographs with rock-salt showing modified reflections.

(12)

(13)

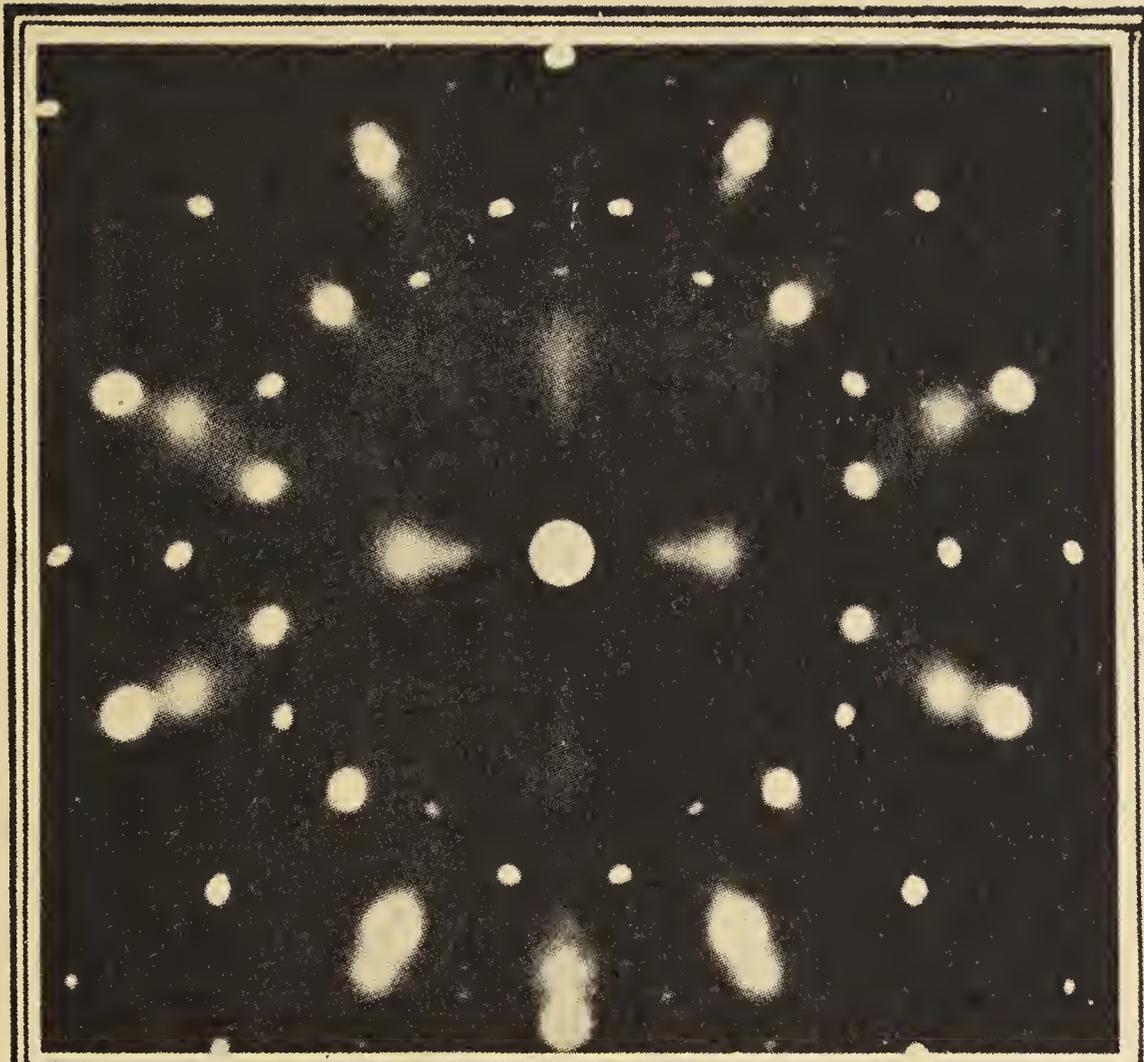


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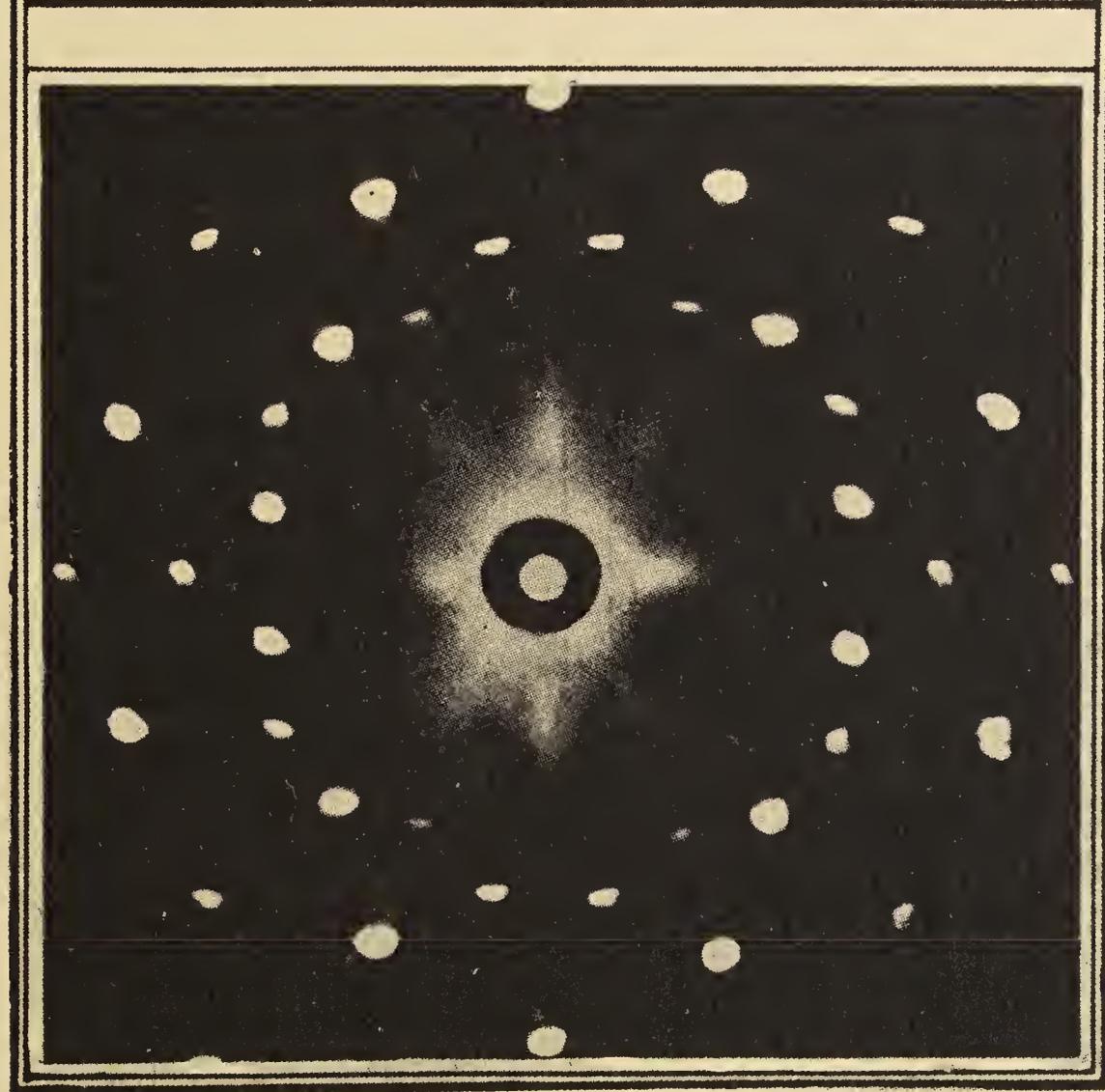
(15)

Figures 12-15. Laue photographs with rock-salt showing modified reflections.

Plate III



(16)



(17)

Figures 16 and 17. Laue photographs with rock-salt showing modified reflections.

Quantum theory of X-ray reflection and scattering— Part I. Geometric relations

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1. Introduction

The simplest example of the optical excitation of the vibrations of a crystal lattice is that afforded by the absorption of infra-red radiations by the crystal. In this case, the material vibrations of the lattice and the electromagnetic waves by which they are excited have the same frequency. When the incident radiations lie in the visible or ultra-violet region of the spectrum, they have a much higher frequency than the possible lattice vibrations, but may nevertheless excite the latter, as is shown by the fact that the light scattered by the crystal includes radiations of diminished frequency. The possibility of excitation in this case is due to the lattice vibrations altering the optical polarisability of the material of the crystal. In both cases, the excitation is essentially an optical process, as is clear from the fact that it occurs irrespective of the temperature of the crystal. That it is also a quantum-mechanical effect is particularly evident in the case of light scattering; the intensity of the lines appearing with diminished frequency in the spectrum of the scattered light is proportional to the Planck constant of action and varies but little with temperature, so long as this is moderate and the lattice vibrations are of sufficiently high frequency.

That the lattice vibrations of a crystal may be excited by X-rays in much the same way as in the case of ordinary light has been suggested and supported by experimental evidence in a recent series of papers in these *Proceedings*.* It was there shown that the character of the resulting phenomena is different in the cases where the lattice vibrations lie respectively in the acoustic and the optical range of frequencies. This is to be expected, because in the vibrations of the acoustic class, the average electron density in the unit cell of the lattice varies periodically while its distribution within the cell remains nearly constant, while on the other hand, in the vibrations of the optical class, the mean electron density in the unit cell

*Raman and Nilakantan, 1940, 11, 379–408.

remains approximately constant while its distribution within the cell varies periodically with time. The possibility of the vibrations of these two classes being induced by the incidence of X-rays therefore arises in different ways. In one case, it is the time-variation of the mean polarisability of the crystal and in the other case the time-variation of the structure amplitudes (Fourier components) of the electron density that is responsible for the excitation of the vibrations. It is not surprising therefore that the effects produced on the incident radiation differ even in respect of their geometric characters in the two cases.

It is proposed in these papers to develop in mathematical form the ideas outlined in the papers quoted above. In this first instalment, the purely geometric aspects of the phenomena will be discussed, the important question of intensities being only touched upon incidentally. The fuller treatment of the latter will be given in part II.

2. The acoustic case

From the remarks made above, it is evident that the cases in which the frequency of the lattice vibrations lie respectively in the acoustic and optical ranges must be considered separately. We shall proceed on the assumption that exchanges of energy and momenta take place between the incident X-radiation and the waves excited by it in the crystal, the substance of the latter otherwise taking no part in the phenomena. The conservation of energy and momentum requires

$$h\nu = h\nu' + h\nu^* \quad (1)$$

$$\frac{\vec{h}}{\lambda} = \frac{\vec{h}}{\lambda'} + \frac{\vec{h}}{\lambda^*} \quad (2)$$

ν , ν' and ν^* being respectively the frequency of the incident and scattered X-rays and of the excited acoustic waves; λ , λ' and λ^* are the corresponding wavelengths. Equation (1) shows that the frequency of the scattered X-rays is diminished relatively to the incident X-rays by the frequency of the sound-waves excited in the process. As, however, ν is far larger than ν^* we may in equation (2) take $\lambda = \lambda'$ without sensible error and proceed to solve it geometrically as shown in figure 1.

With O as centre, we draw a sphere having a radius equal to $1/\lambda$. The particular radius OI of the sphere which is parallel to the incident X-rays being marked out, we draw a second sphere with I as centre and $1/\lambda^*$ as radius which intersects the first sphere along the circle RR. It is evident that the generating lines of the cone ORR represent the possible directions of the scattered X-rays corresponding to the acoustic wavelength λ^* . The semi-vertical angle of this cone ψ is given by the relation

$$2\lambda^* \sin \psi/2 = \lambda. \quad (3)$$

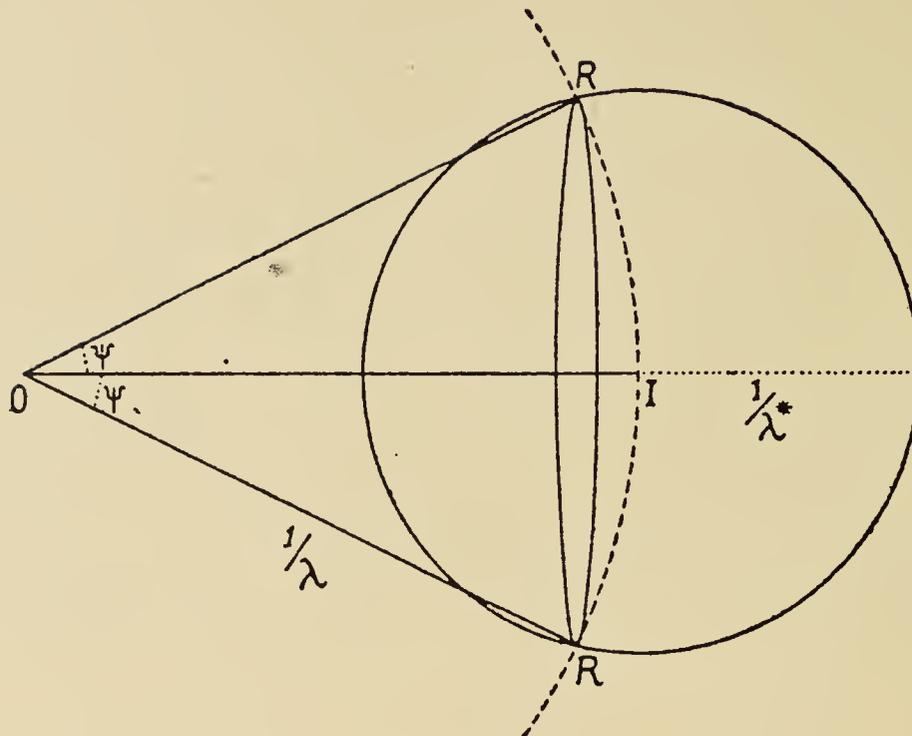


Figure 1

When λ^* is infinite, ψ vanishes and the cone of scattered X-rays collapses to a line along the incident ray. As λ^* diminishes however, the cone opens out, reaching its maximum semi-vertical angle when the wavelength of the acoustic waves is the minimum physically possible in the crystal. In the case of a cubic crystal, this minimum wavelength would certainly be greater than the grating constant of the crystal, and it is clear from (3) that in any setting of the crystal, the directions in which the Bragg reflections by the crystal could be observed would lie outside the cone of monochromatic radiations scattered by it. The distribution of energy in the cone of scattered X-rays is a special problem into which we shall not here enter. It is obvious, however, that if the acoustic spectrum of the crystal has a concentration of energy at or near a particular wavelength which may be greater than the minimum possible, the scattered X-rays may be expected to show a concentration of intensity in the vicinity of a corresponding cone of rays.

3. The optical case

Equations (1) and (2) are equally applicable in the optical case, ν^* being now one of the characteristic optical frequencies of the crystal lattice and λ^* is the wavelength of the periodic stratifications of electron density resulting from the lattice vibrations of that frequency excited in the crystal by the incident X-rays. ν^* is, of course, much larger than in the acoustic case, but even so, it is small compared with the X-ray frequency. Hence, though the change of frequency in the act of reflection indicated by equation (1) is an essential part of the phenomenon, we may without sensible error take $\lambda = \lambda'$ in equation (2). We shall, however,

retain the ascent in λ' to indicate that the vector $1/\lambda'$ refers to the direction of the reflected X-ray. In the acoustic case, the vector $1/\lambda^*$ has an arbitrary direction and an arbitrary magnitude subject to only a maximum limit, with the result that the vector $1/\lambda'$ representing the direction of the scattered X-rays has an arbitrary direction lying within a certain cone. In the optical case, however, conditions are different, as we shall presently see, with the result that the vector $1/\lambda'$ is restricted to specifiable directions and the observed effect is in the nature of a well-defined reflection and not an irregular scattering.

We shall first consider the particular case in which the optical vibrations excited in the cells of the crystal lattice are everywhere of identical phase; in other words, the phase-waves of the lattice vibrations have an infinite wavelength ($\Delta = \infty$). As already remarked, the possibility of optical excitation of the lattice vibrations depends on the fact that these vibrations produce time-periodic variations in the Fourier components of the space distribution of electron density, in other words, produce periodic pulsations of the structure amplitudes of the crystal. When $\Delta = \infty$ the wavelength of these pulsations is the same as that of the crystal spacings, or a harmonic thereof, and the wave-fronts also run parallel to the crystal spacings. Accordingly, we may write

$$\frac{\vec{1}}{\lambda^*} = \frac{\vec{n}}{d}, \quad (4)$$

where n is an integer (1, 2, 3, ...) and $1/d$ is a vector normal to any chosen set of crystal spacings, its magnitude being the reciprocal of that spacing. Combining (2) and (4), we have

$$\frac{\vec{1}}{\lambda} - \frac{\vec{1}}{\lambda'} = \frac{\vec{n}}{d}. \quad (5)$$

Representing this graphically, (figure 2), we derive the formula $2d \sin \theta = n\lambda$, θ being the glancing angle of incidence and of reflection. Equation (5) thus shows that *when the phase-wave length Δ of the lattice vibrations is assumed to be infinite, the quantum reflection of X-rays with diminished frequency occurs under the same geometric conditions as the classical X-ray reflections.*

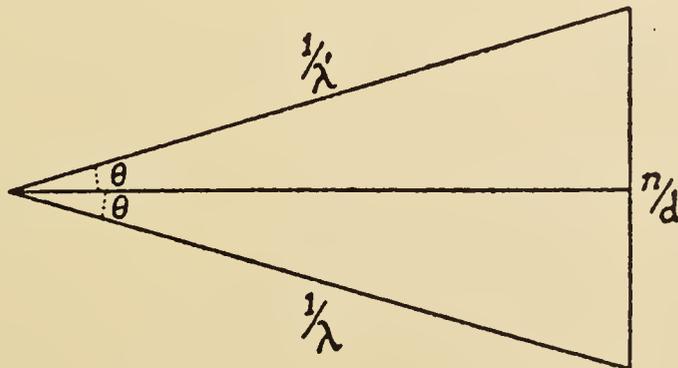


Figure 2

The case when Δ is finite corresponds to a lattice vibration in which the phase of the atomic vibrations alters progressively from cell to cell. The phase of the pulsation of structure-amplitude will therefore also alter from cell to cell, and *in general*, both the direction of the wave-fronts along which this phase is constant, and the spacing between successive such wave-fronts will differ from the crystal spacings. These quantities are indicated by the vector $1/\lambda^*$ and the reciprocal of its magnitude. We may readily find the relation between λ^* , the lattice wavelength Δ and the crystal spacing d/n (see figure 3).

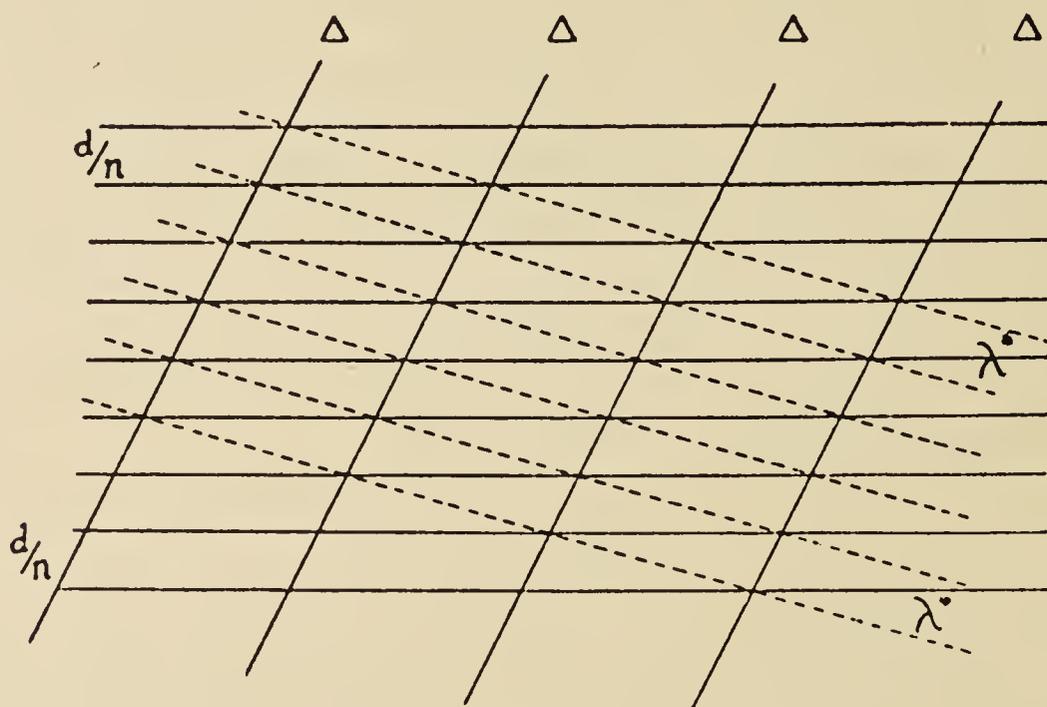


Figure 3

The crystal spacings are a set of equidistant planes marked d/n in the figure and the phase waves of the lattice vibrations are another set of planes marked Δ crossing them at an angle as in figure 3. It is evident that the planes along which the phase of the pulsations of electron density would be constant would be the set of planes crossing both diagonally and marked λ^* in the figure. The spacings of the three sets of planes are evidently connected by the vector relationship between their reciprocals (see note at the end of the paper).

$$\frac{\vec{1}}{\lambda^*} = \frac{\vec{n}}{d} + \frac{\vec{1}}{\Delta}. \quad (6)$$

Combining (6) with (2), we have, in the most general case

$$\frac{\vec{1}}{\lambda} - \frac{\vec{1}}{\lambda'} = \frac{\vec{n}}{d} + \frac{\vec{1}}{\Delta}. \quad (7)$$

Equation (7) reduces, as it should, to equation (5) when Δ is infinite. It states the most general law of the quantum reflection of X-rays which may be put into

words thus: *We combine vectorially the reciprocals of the crystal spacing and of the wavelength of the optical vibrations of the crystal lattice. The reciprocal of the resultant gives the spacing of the dynamic stratifications of electron density and its direction that of their normal: these dynamic stratifications give a geometric reflection of the X-rays with diminished frequency.*

The optical vibrations of a crystal lattice have well-defined frequencies, as is shown by the sharpness of the lines observed in the spectrum of the light scattered by the crystal. The fact that the frequency shifts observed in light scattering have not so far been found to depend appreciably on the angle of scattering is also significant and shows that the lattice frequencies are approximately independent of the lattice wavelengths. Regarding the observed frequencies as due to the characteristic vibrations of the unit cells in the lattice, it is evident that the frequency as observed with an actual crystal would be N -fold degenerate, N being the number of lattice cells in the fragment of crystal used. Actually, the N frequencies should be regarded as forming an aggregate which is densest at the frequency corresponding to an infinite lattice wavelength ($\Delta = \infty$) and rapidly thins out as Δ diminishes. These considerations enable us to understand the effects to be expected on the basis of equation (7). Δ can always be considered as large compared with d/n . Hence, the effect of its appearance in the right-hand side of equation (7) on its scalar magnitude is a small quantity of the first order. It serves, however, to alter the orientation of the wave-fronts of the dynamic stratifications with respect to the crystal spacings. Indeed this would be its only effect if the vectors $1/\Delta$ and n/d are mutually perpendicular, as the resultant of their addition would then be practically n/d . In the limiting case when Δ is infinite, equation (7) shows that the quantum reflection appears under the same conditions as the classical reflection and coincides with it in position. It is also then of maximum intensity, as the N -fold aggregate of optical frequencies of the lattice is densest for infinite values of Δ . As the crystal is tilted away from the setting for the ordinary Bragg reflection, equation (7) shows that Δ must diminish in magnitude, and the intensity of the quantum reflection must therefore fall off in proportion to the diminished density of the aggregate of frequencies for smaller values of Δ . As we shall see presently, the quantum reflection also then separates out from the Bragg reflection and can be observed by itself.

4. Geometric law of quantum reflection

The geometric interpretation of equation (7) is facilitated by first considering a case in which the vector $1/\Delta$ besides being small compared with n/d is perpendicular to it and lies in the same plane with it as the incident X-rays. In this case, it is evident that the result of combining $1/\Delta$ and n/d vectorially is to tilt the reflecting planes in the plane of incidence with respect to the crystal spacings but without any alteration of these spacings. If therefore we consider a case in which

the crystal-spacings are so inclined to the incident monochromatic X-rays that they *cannot* give a Bragg reflection, in other words, when

$$\frac{\vec{1}}{\lambda} - \frac{\vec{1}}{\lambda'} \neq \frac{\vec{n}}{d} \quad (8)$$

they would nevertheless give a quantum reflection according to the formula

$$\frac{\vec{1}}{\lambda} - \frac{\vec{1}}{\lambda'} = \frac{\vec{n}}{d'} \quad (9)$$

where d' has the same magnitude as the crystal spacing d , but its direction has been altered so as to satisfy the vectorial relation (9). This relation indicates that *the incident X-rays give a reflection with diminished frequency in the plane of incidence even when the Bragg reflection is not possible, and that the direction in which it appears with reference to the incident X-rays is unaffected by the setting of the crystal, though as remarked above, its intensity would fall off rapidly as the crystal is turned away from the Bragg setting.*

Equation (9) is represented graphically in figure 4 for two cases in which the crystal has been turned away from the Bragg setting in one direction or the other.

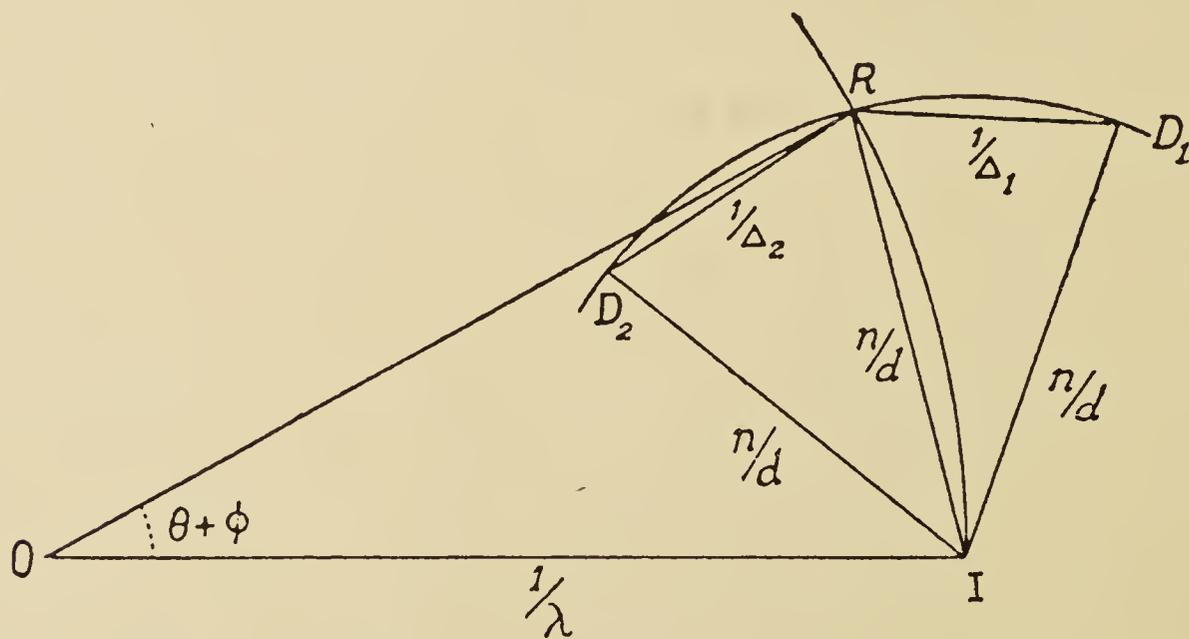


Figure 4

In both cases, the direction of the reflected ray OR is the same and is given by the trigonometric formula

$$2d \sin \frac{1}{2}(\theta + \phi) = n\lambda, \quad (10)$$

where θ and ϕ are the glancing angles of incidence and reflection with respect to the crystal spacings.

The postulate made above which results in the formulae (9) and (10), namely, that the vectors $1/\Delta$ and $1/d$ are perpendicular to each other, physically

interpreted, means that the lattice-waves excited by the X-rays have wave-fronts perpendicular to the crystal spacings giving the quantum reflection. There is good reason to believe that this must be actually the case with most crystals. For, the atomic vibrations which are effective in altering the structure-amplitude of any particular spacing are those in which the displacements are normal to the crystal spacing. If the lattice wave-fronts are parallel to the crystal spacings, the phase of the atomic vibrations would alter as we pass from one spacing to the next, whereas if they are perpendicular to the crystal spacings, the phase of the vibration would change along the crystal spacings but not perpendicular to them. The forces brought into play between the neighbouring cells of the lattice by such phase-changes would obviously be much greater in the former case than in the latter. Accordingly, the N -fold aggregate of frequencies would be spread out over a much wider range of frequencies when Δ and d are parallel than when they are perpendicular. So far as the reflection of X-rays is concerned, therefore, we would be justified in considering only the case where Δ and d are perpendicular and ignoring the case where they are parallel. Equation (10) could then be regarded as the generally valid geometric law for the quantum reflection of X-rays with diminished frequency.

It must be recognised, however, that there may be cases where the considerations set forth above cannot reasonably be expected to be valid. It may, for instance, be possible that the binding forces which hold the crystal lattice together are of such a nature that though the atomic vibrations are normal to the crystal planes under consideration, a change in the phase of such vibrations along the crystal planes may evoke forces and disturb their frequencies quite as much as a change of phase normal to them. In such a case, the postulate that the vectors $1/\Delta$ and $1/d$ are perpendicular may cease even to be approximately true. In such cases, that is, when the effective lattice-waves have an arbitrary inclination to the crystal spacings, an alternative principle suggests itself giving the selection rule for the vector $1/\Delta$, namely, that the direction of the vector is such that its scalar magnitude necessary to satisfy equation (9) is a minimum. Such a principle would not be unreasonable in view of the remark already made that the frequency-aggregate of the optical vibrations becomes rapidly less dense for increasing values of Δ . It can readily be shown that this principle gives the same result as equation (10) when θ and ϕ are nearly equal to each other, that is to say when the setting of the crystal is not far from the Bragg position. More generally, however, it deviates from that result.

Figure 5 represents equation (7) graphically for two cases in which the crystal has been turned away from the Bragg setting in one direction or the other, and Δ is chosen to have the minimum necessary length required to satisfy the equation. The direction of the reflected ray is OR_1 in one case and OR_2 in the other. It will be noticed that the effective resulting spacing is in one case greater than d/n , and in the other case less than d/n . At the correct Bragg setting, therefore, OR_1 and OR_2 become coincident. The geometric law of the quantum reflection is seen

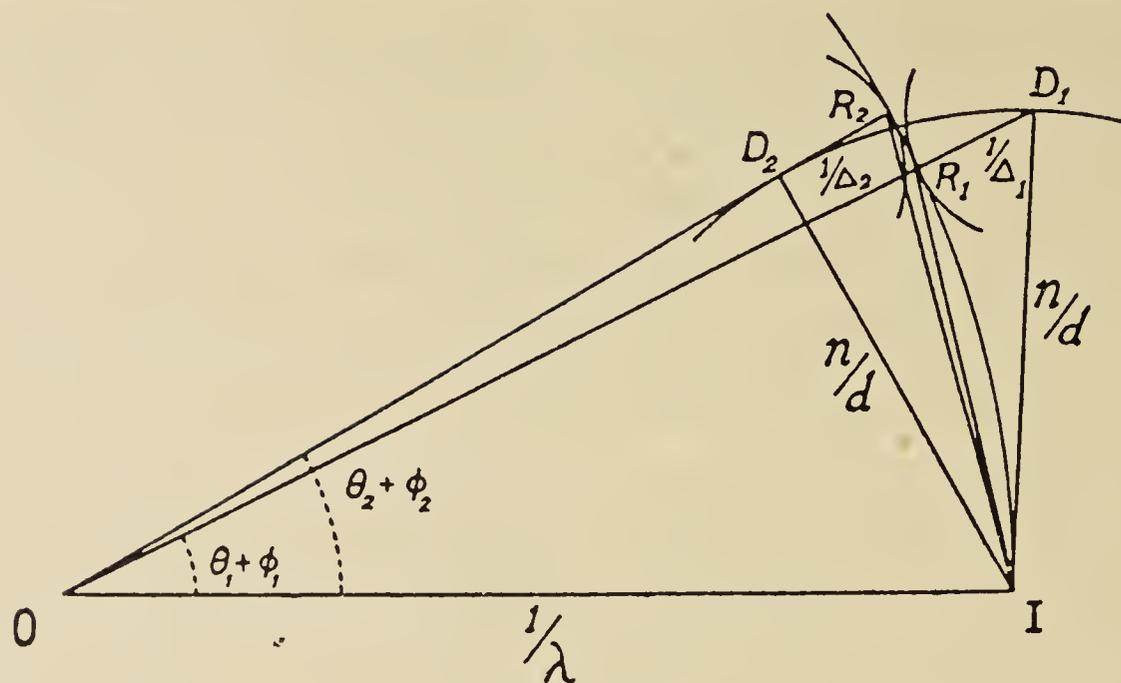


Figure 5

from figure 5 to be

$$d \sin(\theta + \phi) = n\lambda \cos \phi. \quad (11)$$

Equations (10) and (11) give results which differ the more widely, the greater the difference between θ and ϕ , but become identical when $\theta = \phi$. It will be noticed that they correspond respectively to the results which have been found experimentally valid for the cases of sodium nitrate and diamond. The divergence between the results given by the two formulae when $\theta \neq \phi$, and the fact that they have been derived on quite different considerations suggests that when the crystal is tilted away from the correct Bragg setting, the definition of the quantum reflection should progressively deteriorate. Such an effect is actually observed, but whether it is due solely to the cause stated or is due partly also to other disturbing effects, e.g., thermal agitation or the mosaic structure of the crystal, is a matter for further investigation.

Summary

When X-rays fall upon a crystal, the characteristic vibrations of the crystal lattice may be excited thereby, in much the same way as in the phenomenon of the scattering of light in crystals with diminished frequency, the excitation being a quantum mechanical effect. From the equations for the conservation of energy and momentum, the geometrical relations entering in this effect are deduced theoretically for the two cases in which the lattice vibrations fall within (1) the acoustic range of frequency and (2) the optical range. In the first case, the incident X-rays are scattered in directions falling within a cone having the incident ray as axis and with a semi-vertical angle $2 \sin^{-1} \lambda/2\lambda^*$ where λ^* is the minimum

acoustical wavelength. In the second case, we have a quantum-mechanical reflection of the X-rays with diminished frequency in a direction which generally follows the geometric formula $2d \sin \frac{1}{2}(\theta + \phi) = n\lambda$ where θ and ϕ are the glancing angles of incidence and reflection on the crystal spacings. For crystals with specially rigid bindings, the alternative formula $d \sin(\theta + \phi) = n\lambda \cos \phi$ is indicated as being more appropriate. In either case, the intensity of the reflection should fall off rapidly as θ and ϕ diverge.

Note: Equation (6) may be very simply derived from the construction shown in figure 3. The vector sum of the two sides of a triangle is equal to the third side. Dividing this equation by the area of the triangle, we get a vector relation between the reciprocals of the three perpendiculars from the vertices on the sides.

The two types of X-ray reflection in crystals*

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1. Introduction

One of the most remarkable and fruitful discoveries in modern science was made when Max von Laue applied the principles of the wave-theory to find the effect of passage of a pencil of X-rays through a crystalline plate and arrived at conclusions which were strikingly confirmed by experiment. When the pencil after traversing the crystal is received on a photographic plate, we find recorded on the plate, as predicted by Laue, numerous spots in geometric array, their positions being closely related to the internal atomic architecture of the crystal and the direction of passage of the incident X-rays. The location of the spots in the Laue pattern is determined by the consideration that the secondary radiations from the atoms in the crystal co-operate in the directions indicated by the spots by reason of an agreement in phase, such agreement being itself a consequence of the arrangement of the atoms in a regular space-lattice. The Laue conditions which express this situation are mathematically equivalent to the Bragg formula; the latter follows very simply from the consideration that the crystal is a regularly stratified medium and should, therefore, selectively reflect the radiations falling on its strata at an angle of incidence appropriate to their spacing and to the wavelength of the X-rays in accordance with a general principle familiar to students of optics.

Laue's discovery was a vindication of the wave-theory and was naturally regarded as finally settling the issue, then being keenly debated, whether X-rays were corpuscles or waves, in favour of the latter hypothesis. Actually, however, the position is not quite as simple as this. As we know at the present time, there is an essential duality in the behaviour of the fundamental physical entities. They

*The new type of X-ray reflection forming the subject of this paper was first described and an explanation of it on the basis of the quantum theory given in a series of papers published earlier this year by Raman and Nilakantan in these Proceedings and elsewhere. The present report is intended to be a self-contained theoretical exposition of the subject and incorporates the ideas already expounded in the papers by Raman and Nilakantan, as also the fuller mathematical treatment by Raman and Nath published in these Proceedings for July 1940. Recent experiments by Nilakantan with diamond completely establish the quantum theoretical explanation of the phenomenon.

have a wave-aspect as well as a particle aspect, and these two characters are complementary and not contradictory. To get a complete picture of the observable phenomena, therefore, we can ignore neither one aspect nor the other. It is thus necessary to bear in mind the particle aspect as well as the wave-aspect of the Laue phenomena, and indeed, when we approach the subject from this point of view, the possibility of there being two distinct kinds of X-ray reflection becomes apparent. From the particle point of view, the X-ray reflections of the Laue type are *elastic* collisions of the photon with the crystal lattice, while from the wave-point of view, they arise from the fact that the crystal has a static periodicity of structure. This suggests that a second type of X-ray reflection in crystals should be possible, that from the particle stand-point is an *inelastic* collision in which the photon gives up a part of its energy during the encounter and excites the vibrations of the crystal lattice, while from the wave-standpoint, the reflection is due to the *dynamic stratifications of density* arising from such vibrations of the lattice. From either point of view, a change of frequency is seen to be a necessary feature of the second type of X-ray reflection; we may, therefore, refer to it as the quantum or modified reflection to distinguish it from the classical or unmodified reflections.

2. Theory of modified reflection

We may now proceed to consider a little more closely the mechanism of the modified X-ray reflection and its relation to the structure of the crystal. The classical or unmodified X-ray reflections arise from the fact that the electron density in the crystal is a periodic function of the co-ordinates in three dimensions. The intensity of the reflection by any particular set of crystal planes is determined by a quantity known as its structure amplitude which specifies the variation of the mean electron density over a plane when such plane is moved normally to itself through the crystal. The positions occupied by the atoms in the unit cell of the lattice are the most important factor in determining the structure amplitudes, though other factors such as the number of electrons and the distribution of electron density in each atom also enter into it.

With scarcely an exception, the actual crystals with which we are concerned contain more than one atom per unit cell, indeed usually several atoms of the same or of different kind. These atoms are held together in their places as the result of forces acting between each atom and its neighbours. Each individual atom is capable of vibrating about its position of equilibrium, but in view of the existence of the interatomic forces, it is more appropriate to consider the crystal lattice as a whole and to fix our attention on some one or another of its possible modes of vibration. These modes fall into two divisions, namely, the vibrations of the acoustic type and those of the optical type. The vibrations of the acoustic class lie for the greater part in the lower ranges of frequency, while the optical

vibrations have frequencies falling in the infra-red region of the spectrum. The character of the movements involved in these two classes differs essentially. The acoustic vibrations consist chiefly of translatory movements of the unit cells of the lattice relative to each other, while in the vibrations of the optical class the atoms within each unit cell oscillate relatively to each other about their common centre of gravity. The interatomic displacements within the unit cells for the acoustic vibrations and the translations of the unit cells for the optical vibrations are in each case of relatively minor importance.

We may now fix our attention on the optical vibrations of the crystal lattice and consider their effect on the structure amplitudes responsible for the X-ray reflections. In the first instance, we may make the simplifying assumption that the oscillation in all the unit cells is of the same frequency, amplitude and phase. It is evident that with this restriction, the atomic vibrations do not affect the uniformity of the crystal structure; the spacing and orientations of the crystal planes remain completely unaltered. The structure amplitudes of the crystal, however, alter periodically with time to an extent depending on the magnitudes and directions of the atomic displacements of which only the components normal to the spacing under consideration are effective. It is evident that the electronic density in the crystal would in these circumstances exhibit two different kinds of space variation, a static structure amplitude which is not a function of time, and a dynamic structure amplitude which varies with time and has the same frequency as the optical vibration of the crystal lattice. If the vibration of the lattice is sufficiently intense, the existence of a dynamic structure amplitude should evidently result in an alteration of the static structure amplitude, in most cases making it smaller than what it would be in the absence of such vibration.

From optical theory, it is evident that a dynamic structure amplitude would result in sharply defined monochromatic reflections in the same way as a static structure amplitude, except that the reflections would now occur with a change of frequency. Since under the assumptions made, the dynamic structure amplitudes do not differ from the static ones in respect of their spacings and orientations, the geometric conditions necessary for the observation of the static and dynamic reflections would also be identical, in other words, these reflections would either appear or not appear together in the same circumstances. If, for instance, the incident X-radiation be monochromatic, neither the modified nor the unmodified reflection would be observable unless the Bragg condition is satisfied.

3. Geometric law of modified reflection

We may now remove the restrictive assumption made that the atomic oscillations occur in identically the same phase in all the unit cells comprising the crystal. The oscillation will be assumed to have the same frequency and amplitude everywhere, but its phase will be regarded as variable from cell to cell. While this

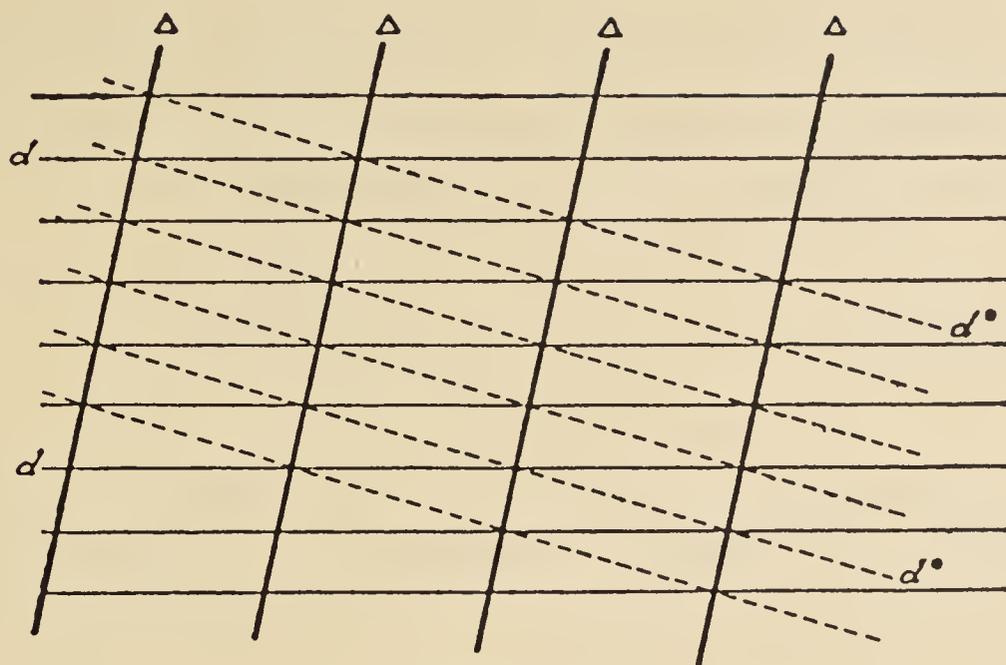


Figure 1

variation of phase would not affect the *static structure amplitudes* giving the unmodified reflections, it would profoundly influence the *dynamic structure amplitudes* and the effects produced by them. This is very readily seen from the accompanying diagram (figure 1), in which the thin lines represent a set of crystal planes and therefore also the planes among which the time-variations of electron density would be the same if the phase of the atomic vibrations were everywhere identical. The heavy lines crossing these at an angle represent the planes along which the phase of the atomic vibrations is constant. It is then evident that the dynamic stratifications of electron density would be along the diagonal planes cutting through the crystal spacings and the phase wave-fronts of the atomic vibration. These diagonal planes are indicated by the dotted lines in the figure, and their spacing and orientation are given by the vectorial formula:

$$\frac{\vec{1}}{d^*} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta} \quad (1)$$

Here d^* is the spacing of the dynamic stratifications of electron density, d is the static crystal spacing, and Δ the spacing of the phase-waves of the atomic vibration in the crystal lattice. Equation (1) shows that in the limiting case when Δ is infinite, d^* becomes identical with d both in magnitude and direction. The classical and quantum reflections then coincide as already remarked.

So far as the optics of the cases is concerned, the classical and quantum reflection are on a similar footing. For the former to occur, the Bragg condition, namely,

$$2d \sin \theta = n\lambda, \quad (2)$$

must be satisfied, while for the quantum reflections it is similarly necessary that

$$2d^* \sin \psi = n\lambda, \quad (3)$$

θ and ψ being the glancing angles of the incident beam on the static and dynamic stratifications measured in the respective planes of incidence. Denoting by ϑ and ε , the angles which the crystal planes make respectively with the phase-waves and with the dynamic stratifications, we have from equation (1) and figure 1,

$$d^* \sin \vartheta = d \sin (\vartheta + \varepsilon) = \Delta \sin \varepsilon. \quad (4)$$

Substituting the first of these relations in (3), we obtain,

$$2d \sin \psi \sin (\vartheta + \varepsilon) = n\lambda \sin \vartheta. \quad (5)$$

From equation (4), we see that if the wavelength Δ is large compared with the crystal spacing d or the dynamic stratification d^* , the angle ε would be small compared with ϑ or $(\vartheta + \varepsilon)$. Hence, provided ϑ is not nearly equal to 0 or π , we may write (5) in the *approximate* form

$$2d \sin \psi = n\lambda, \quad (6)$$

which, it will be seen, is merely (3) with d written for d^* , that is to say, with the spacing of the dynamic stratifications put equal to that of the crystal planes from which they are derived. *Equation (6) is the same as equation (2) with ψ written for θ and is thus the geometric law for quantum reflections analogous to the Bragg law for the classical reflections.* Since the angular separation between the incident beam and the quantum reflection is 2ψ , equation (6) indicates that within the limits of its validity, *the angular separation of the quantum reflection and the incident beam is independent of the setting of the crystal and is equal to the angular separation of the classical reflection from the incident beam at the Bragg setting of the crystal.*

If Δ is infinite, it follows from (4) that $\varepsilon = 0$ and the approximate equation (6) becomes identical with the rigorous equation (5). How nearly this continues to be true when ε is finite depends on the angle ϑ . If $\vartheta = \pi/2$, $\sin \vartheta = 1$ and differs little from $\sin (\vartheta + \varepsilon)$ even when ε is as much as $\pm 10^\circ$. *Hence, for the particular case in which the phase wave-fronts are transverse to the crystal planes, the simple formula (6) may be regarded as practically the rigorous geometric law of quantum reflection.* If, however, the inclination ϑ of the phase wave-fronts to the crystal planes is much less than $\pi/2$, it is not permissible to write $\sin \vartheta = \sin (\vartheta + \varepsilon)$ except for very small values of ε , and hence in such a case, the rigorous formula (5) should be employed. It is evident that the angular separation 2ψ of the quantum reflection from the incident beam would not then be independent of the crystal setting, but would be greater or less than the fixed value given by equation (6) according as ε is negative or positive, that is to say, according as the tilt of the dynamic stratifications with respect to the crystal planes is one way or the other.

The static and dynamic reflecting planes are coincident when Δ is infinite and ε is therefore zero. The planes of incidence for both reflections are, therefore, identical in this particular case. If this result be true generally, *it would follow that the quantum reflection by any particular crystal spacing appears in the same plane of incidence as the usual Laue reflection.* We may then write $2\psi = (\theta + \phi)$ and

$2\varepsilon = (\phi - \theta)$, ϕ being the glancing angle of the quantum reflection measured with reference to the crystal planes. Equation (5) then becomes

$$2d \sin \frac{\phi + \theta}{2} \sin \left(\vartheta + \frac{\phi - \theta}{2} \right) = n\lambda \sin \vartheta, \quad (7)$$

while equation (6) takes the form

$$2d \sin \frac{1}{2}(\phi + \theta) = n\lambda. \quad (8)$$

It is easily seen that the rigorous formula (7) would in every case give values of ϕ closer to θ than the approximate formula (8), the difference being least when $\vartheta = \pi/2$. In general, therefore, when ϑ is less than $\pi/2$, *the quantum reflection is nearer the Laue reflection than the fixed position indicated by the approximate formula; it moves in the same direction as the Laue spot, though much more slowly, as the crystal is rotated; it coincides with and is overtaken by the Laue spot at the Bragg setting and continues to follow its further movement as the crystal is turned away from that setting.* In the limiting case when $\vartheta = 0$, equation 7 indicates that $\phi = \theta$, in other words, the quantum reflection appears superposed on the Laue spot.

4. Intensity of modified reflection

The modified reflection is the result of the crystal taking up a quantum of energy $h\nu^*$ and the photon going off with the remainder of the energy $h(\nu - \nu^*)$, ν and ν^* being the frequency of the incident radiation and of the lattice vibrations respectively. The energy $h\nu^*$ being shared by all the lattice cells in the crystal, the amplitude of vibration and the resulting dynamic structure amplitude would be exceedingly small. It might, therefore, seem at first sight that the probability of the process occurring would be negligible. Actually, however, the small probability of the individual process is set off by the fact that the number of lattice cells N in the crystal is enormously large, and the system therefore possesses N discrete frequencies of vibration ranging around the value ν^* . The fraction dN/N of this large number which becomes effective in any particular circumstances determines the observed intensity of the quantum reflection. This fraction should clearly be a function of the magnitude and direction of the phase vector $1/\Delta$ which we shall denote for convenience by the symbol δ . We may, therefore, write

$$dN/N = \frac{1}{4\pi} G(\delta, \chi, \vartheta) \sin \vartheta d\vartheta d\chi d\delta. \quad (9)$$

In this equation, ϑ is the angle already introduced, namely the inclination of the phase wave-fronts to the crystal strata. χ is the azimuth of a plane normal both to the crystal strata and to the phase wave-fronts, the reference plane for which $\chi = 0$

being the plane of incidence on the crystal strata. $\sin \vartheta d\vartheta d\chi$ is, therefore, the elementary solid angle within which the vector δ lies.

The dependence of the G -function upon the value of δ should evidently be very pronounced. Since the characteristic frequency ν^* corresponds to a zero value of δ , we may expect the possible degrees of freedom to cluster densely around small values of δ and to thin out for large values of δ . In other words, the G -function would have a strongly marked maximum when $\delta = 0$ and diminish rapidly as δ increases. If, therefore we regard the other variables in the function as having fixed values, e.g., $\chi = 0$ and $\vartheta = \pi/2$, the variation of intensity of the quantum reflection would depend solely on the value of δ determined by the angles of incidence and reflection. It would then follow from equation (1) that *the intensity of the quantum reflection would be a maximum at the Bragg setting of the crystal for which $\phi = \theta$ and would fall off rapidly as the crystal is moved away from this setting in either direction.*

It will be noticed that we have written the G -function with the angles χ and ϑ appearing explicitly in it, thereby indicating that the number of degrees of freedom lying between given limits of δ depends on the inclination of the wave-fronts to the crystal planes and also on the azimuth of the plane which is normal to both the static and dynamic stratifications of density. Such a dependence is to be expected on dynamical grounds. It is well known that in a crystal, the relation between wavelength and frequency for vibrations of the *acoustic class* is a function both of the direction of vibration and the direction of propagation, the wave-front splitting up into a surface of three sheets even in a cubic crystal. There would, therefore, be no justification for assuming that for vibrations of the optical class, the distribution of the degrees of freedom would be independent of either the orientation of the wave-fronts in the crystal, or of the directions of the atomic vibration in them. In our present problem, we are concerned with the modes of vibration in which the displacements of the atoms are predominantly normal to the particular crystal planes under study, since displacements parallel to the planes have no effect on their structure amplitudes. We may, therefore, reasonably anticipate that the G -function should show a strongly marked dependence on the angles ϑ and χ which enter in our problem.

It is evident that if the angles ϑ, χ defining the orientation of the phase-waves are regarded as entirely arbitrary, the optical conditions necessary for a reflection of the X-rays would be insufficient to indicate a unique direction for such reflection for any given setting of the crystal. It is, however, easily shown analytically or geometrically that they suffice to indicate a direction which would correspond to a minimum value of δ and therefore also to a maximum observable intensity of reflection, the values of χ and ϑ corresponding to such direction being 0 and $(\pi/2 - \phi)$ respectively. The zero value of χ indicates that the reflection would be in the plane of incidence, while the value $(\pi/2 - \phi)$ on substitution for ϑ in (7) yields the formula

$$d \sin(\phi + \theta) = n\lambda \cos \phi, \quad (10)$$

which may also be written as

$$d(\sin \theta + \cos \theta \tan \phi) = n\lambda, \quad (11)$$

both reducing to the Bragg formula when $\theta = \phi$.

The considerations on which equation (11) is based would, however, be invalid and the results given by this formula would be contradicted by experiment, if the angles ϑ and χ appear explicitly in the distribution function $G(\delta, \chi, \vartheta)$ as assumed in our equation (9). For, when this is the case, the maximum of this function would be determined, not solely by the variations of δ , but also by the independent variations of χ and ϑ , and the preferred values of these angles which make the G -function a maximum must, therefore, influence both the intensity of the modified reflection as well as the plane and direction in which it is observed. The value of χ determines the plane of reflection, while that of ϑ notably influences the direction of reflection in that plane. Hence the more precisely these angles can be specified, the more sharply defined would the direction of reflection be. The dependence of the distribution function on the angle variables thus plays an important part in determining all the observable features of the quantum reflection, namely, the plane and the direction in which it is to be found, its sharpness and its intensity. The preferred value of ϑ is in particular of special importance and may be expected to depend on the substance chosen for investigation and possibly even on the particular set of crystal planes from which the reflections are observed. It may be evaluated by observing the quantum reflections over a sufficiently wide range of settings of the crystal and comparing the experimental results with the general formula (5) or its near equivalent (7).

5. Effect of acoustic vibrations

We may now briefly discuss the phenomena resulting from the excitation of those crystal vibrations which lie in the acoustic range of frequency. When the number of atoms in the unit cell of the lattice is fairly large, the proportion of the aggregate number of degrees of freedom appearing as acoustic vibrations is small and the effects due to them are of small importance compared with those arising from the optical vibrations. Nevertheless, they deserve some consideration. The distinguishing feature of the acoustic vibrations is that they involve translatory movements of the unit cells, in other words a disordering of the crystal lattice, while the optical vibrations involve such movements to a negligible extent and may, therefore, be excited without distorting the crystal lattice. We have already noticed the latter as the special feature which enables the crystal to give modified or quantum reflections. We shall presently see that no such reflections would result from crystal vibrations of the acoustic class, and that on the contrary these vibrations would give rise only to a diffuse scattering of the X-rays.

A longitudinal sound-wave causes the mean electronic density in a crystal to

vary periodically, and if its wavelength is sufficiently large in relation to the spacing of the lattice planes, we may ignore the latter and regard the wave itself as a time-periodic stratification of electronic density. Accordingly, the X-ray photon impinging on the crystal should excite such sound waves by inelastic collision and itself be reflected in the process, provided that the length Δ of the sound-wave, the glancing angle θ on its wave-fronts and the X-ray wavelength λ satisfy the relation

$$2\Delta \sin \theta = \lambda. \quad (12)$$

Accordingly, since both Δ and θ are arbitrary, the effect here contemplated would give rise to a diffuse scattering in directions surrounding the incident beam and lying within a cone of semi-vertical angle 2θ determined by the limiting value of θ at which the argument fails, namely, when Δ is of the same order of magnitude as the lattice spacings in the crystal.

To find the phenomena in directions lying outside this cone, the procedure to be followed would be formally analogous to that indicated earlier for the optical vibrations, namely, to analyse the structure amplitudes of the crystal into a static part and a dynamic part having the frequency of the acoustic vibration, and to consider the effect of the latter separately. The detailed results would, however, be quite different from those obtained for the optical vibrations. While an infinite wavelength Δ for the optical vibrations corresponds to one or other of the characteristic frequencies at which there is a maximum concentration of the degrees of freedom of the system, we have exactly the opposite situation in the acoustic case, the infinite wavelength then corresponding to zero frequency and a minimum concentration of the degrees of freedom. Hence the arguments which indicate that in the optical case the reflected beam is limited to particular directions in the plane of incidence are wholly inapplicable for the acoustic vibrations.

We conclude that *the acoustic vibrations of the crystal lattice, though they may be excited by an inelastic collision of the photon, give rise to a diffuse scattering without any pronounced directional effects.*

6. Analogy with light scattering

As is well known, when monochromatic light traverses a crystal and the light diffused by it is spectroscopically examined, the scattered radiations exhibit diminished and in some cases also enhanced frequencies. The frequency shifts fall into two classes. Some of them are very small and require for their observation the use of a Lummer–Gehrcke plate or a Fabry–Perot etalon; the shifts are found to depend on the direction of observation and evidently arise from the acoustic vibrations of the crystal lattice. The second group of frequency shifts may be observed with an ordinary spectroscope and correspond to those optical

vibrations of the crystal lattice which are active in light scattering. In the latter case, no variations with the direction of observation have been reported, though no very careful investigations appear to have been made on this question.

It is recognised that the scattering of light with change of frequency is a quantum effect, though it has a classical analogue which fails to represent the observed facts in essential particulars. There is thus a clear analogy between the modified scattering of light and the quantum reflection of X-rays, both phenomena arising from the inelastic collisions of photons with crystals. The wavelength of the incident radiation is widely different in the two cases, and this is largely responsible for the difference in the character of the resulting effects. Despite the obvious differences, the fundamental similarity in the processes involved and the phenomena observed should be useful as a guide to research in both fields of investigation. In particular, it is desirable to emphasise that, as in the case of X-rays, the change of frequency observed in light-scattering should be regarded as the co-operative effort of extended domains in the crystal and not the effect of the individual ions or molecules in it.

In the literature of light-scattering, we are familiar with the idea that certain optical modes are active while others are inactive, the distinction being largely determined by the symmetry characters of the vibration. In the X-ray problem, the question whether an optical vibration is 'active' in giving a modified reflection depends on whether it modifies the structure amplitude of the particular crystal spacing under study. It is evident, however, that in the X-ray problem we are dealing with the superposed effect of all the characteristic optical modes, and cannot isolate the effect of any one of them in particular. On the other hand, we can observe the modified reflection from numerous individual crystal planes and the geometric relation of such planes to the various optical modes of vibration of the lattice cells would naturally be different. The X-ray method is also capable of application to crystals with which optical study is difficult or impossible. Hence a study of the phenomena of the modified X-ray reflection may be expected to lead us to a deeper understanding of the problem of crystal physics, and to supplement in important respects the results of spectroscopic studies.

7. Influence of temperature

The analogy with light scattering is particularly useful in considering how the intensity of modified X-ray reflection would be influenced by varying the temperature of the crystal. As is well known, the character of the phenomena observed in light scattering differs essentially in the two cases in which $h\nu^* \gg KT$ and $h\nu^* \ll KT$ respectively. In the first case, the thermal agitation of the system plays an insignificant role, and the scattering is due to its transitions from the lowest to higher energy-levels induced by the incident radiation. Hence, the

scattering is with diminished frequency only, and its intensity is independent of temperature, being much greater than that indicated by classical considerations for a vibration with energy KT . In the second case in which $h\nu^* \ll KT$, the observed effects are practically describable in terms of the classical theory: the intensity of the scattering increases in proportion to the absolute temperature and appears to an equal extent with diminished and with increased frequencies. In the intermediate cases when $h\nu^*$ and KT are of comparable magnitudes, the scattering with diminished frequency is of greater intensity than that with increased frequency. The ratio of the two tends to approach unity as the temperature is raised, and the absolute intensities of both types of scattering also become larger. This is because the transition probabilities from a thermally excited state are greater than from the ground state of the system.

We may naturally expect very similar results in the case of modified X-ray reflection, except that as it is not possible to separate the reflections with diminished and increased frequencies, we are only concerned with the result of their summation. As indicated by the theory, the nature of the results would depend on the characteristic optical frequencies of the crystal. At sufficiently low temperatures, the indications of the classical theory should in every case fail completely, and the quantum reflections, instead of vanishing, should continue to be observable. Further, for crystals with high characteristic frequencies, the intensity of reflection should be much greater than that indicated by the classical considerations, and its increase with rise of temperature should also be slower. On the other hand, for crystals with relatively low characteristic frequencies, the increase of intensity with temperature should be very marked. Further, since this increase indicates a larger population of thermally excited states and therefore also a diminution of the static structure amplitudes, *the increase of intensity of the modified X-ray reflections with rise of temperature would be accompanied by a falling off in the intensity of the unmodified reflections.*

It follows from the foregoing remarks that theories of the temperature effect in X-ray diffraction based on classical considerations cannot be expected to be in full accord with the facts either at low or high temperatures. This is indeed evident from the published literature of the subject. In the treatments usually given, however, the classical considerations are modified by taking into account the zero-point energy of the vibrations of the crystal and assuming that these have an optical effect analogous to that of thermal agitation. The static structure amplitudes of the crystal at low temperatures are thereby brought into better accord with the observed facts. It is evident, however, that except in regard to the classical or unmodified reflections, the effects produced by the crystal on the incident radiation depend on the change in the energy-state of the crystal and not upon its initial energy. The zero-point energy is therefore not really relevant to the discussion of such effects.

8. Summary

The X-ray reflections of the Laue type are elastic collisions of the photons with the crystal considered as a structure with static space periodicities. The modified or quantum reflections are inelastic collisions in which the photon excites the vibration of the crystal lattice and is itself reflected by the dynamic stratifications of electron density arising from such vibrations. The quantum reflections obey the Bragg principle with respect to the dynamic spacings, these however, in general, differing from the static spacings, besides being differently oriented, except when the incidence on the static spacings is at the Bragg angle for the given monochromatic radiation, in which case they are identical. The general geometric formula for the quantum reflection is

$$2d \sin \frac{\phi + \theta}{2} \sin \left(\vartheta + \frac{\phi - \theta}{2} \right) = n\lambda \sin \vartheta,$$

where θ and ϕ are the glancing angles of incidence and reflection, and ϑ is the inclination of the phase-waves to the crystal spacings. If ϑ does not differ greatly from $\pi/2$, this reduces approximately to the symmetric formula $2d \sin \frac{1}{2}(\theta + \phi) = n\lambda$. All the observable features of the quantum reflection are determined by the properties of the G -function which gives the distribution of the degrees of freedom of optical vibration as determined by the reciprocal of the length of the phase-waves of the optical vibration of the lattice and the angle variables ϑ , χ defining their orientation. The dependence on temperature of the intensity of quantum reflection is very different in the two cases where $h\nu^* \gg KT$ and $h\nu^* \ll KT$ where ν^* is the optical frequency of the lattice vibration. The increase of intensity of the modified X-ray reflections with rise of temperature is accompanied by a falling off in the intensity of the unmodified reflections from the same spacings.

Crystals and photons*

SIR C V RAMAN

My first duty on this occasion is to express our gratitude to the authorities of the Andhra University for their generous sympathy and support to the work of the Academy and the opportunity they have afforded us of having our Annual Meeting in a truly academic atmosphere set amidst the beautiful scenery of Waltair. We appreciate very much the warmth of the welcome we have received. Our gathering here gives the Fellows of the Academy an opportunity of visiting the Andhra University at a time when many new developments are receiving attention, and of meeting men like Professor Bhagavantam, Professor Seshadri and Dr Nagendra Nath, whose research papers have filled the pages of the *Proceedings* of the Academy and whose work has shed lustre on the University. They have, like our many other Fellows in other parts of India, given ungrudgingly of their time and energy for the welfare of the Academy. Our special thanks are due to them and other local Fellows and to the Chairman and members of the Reception Committee for having worked to make this meeting a success.

In my Presidential Address last year at Bangalore, a long-term programme of research on the physics of crystals was outlined and put forward as likely to yield valuable results for our knowledge of the solid state. Looking over the *Proceedings* of the Academy for the last twelve months, I find that fourteen papers on crystal physics (listed at the end of this address) have appeared in it, of which three are from Waltair and the rest from Bangalore. We have no reason to be dissatisfied with the progress made so far, and indeed it may be claimed that some of these papers deal with the problems of the solid state from a quite novel standpoint and open up new pathways of investigation. I propose in this address to survey broadly the field of research dealt with in these papers which may be designated as the newer crystal optics based on the ideas of the quantum theory, to distinguish it from the older optics which considers the effects of passage of radiation through crystals on the wave-principles. The quantum optics links together the phenomena observed with infra-red radiation, visible light and X-rays in a remarkable way, and reveals the existence of a new type of X-ray reflection in crystals.

* Presidential Address delivered at the Annual Meeting of the Indian Academy of Sciences held on the 27th December 1940, at the Andhra University, Waltair.

As is well known, the behaviour of a crystal with respect to common light is intimately related with the geometric symmetry of the system to which it belongs. Rock-salt and diamond, for example, which are cubic crystals are isotropic or singly refracting; calcite and sodium nitrate which are rhombohedral crystals are doubly refracting but optically uniaxial; aragonite and barite which are orthorhombic are doubly refracting but optically biaxial. These characters of the respective crystals are determined by the optical polarisability of the substance in different directions. The polarisability may be geometrically represented by a surface which is a sphere for an isotropic crystal, a spheroid of revolution for a uniaxial crystal, and an ellipsoid with three unequal axes for a biaxial crystal. The polarisability is a bulk or molar property, which is intimately connected with the atomic architecture of the crystal, that is to say, by the properties of the atoms or ions or molecules composing the crystal, and by the manner in which they are spaced, orientated and linked together. The modern techniques for growing large crystals enable us to study and exhibit the very striking optical behaviour of many common substances. Sodium nitrate, for instance, can be grown into large crystals, and a block of it shows a birefringence which is even more obvious and striking than that of calcite. Still better is naphthalene which is a biaxial crystal and shows an extremely large birefringence. *The angles of internal and external conical refraction of naphthalene are about 14° , and are thus eight times larger than those of aragonite with which conical refraction is usually exhibited.* Needless to say, conical refraction as observed with a piece of naphthalene is far more striking than that exhibited by aragonite. As was shown by Bhagavantam in the very first paper he published as a research student, the strong birefringence of naphthalene is closely connected with the very great optical anisotropy of the molecules as well as the special orientation of the molecules in the crystal.

The classical optics of crystals prefers to ignore the atomic architecture of the solid and regards the substance as a continuum with specific molar properties. The crystal functions as a pathway for the passage of the radiation, taking part in its propagation but remaining essentially undisturbed in the process. Even when, as frequently happens, the radiation is partially absorbed by the crystal, this is fitted mathematically into the wave-picture by making the optical constants of the substance complex quantities instead of real numbers. Such a wave-picture is a satisfactory description of the phenomena which it is intended to cover. But it is not a complete description of the facts. This was shown clearly by the studies on the scattering of light in crystals commenced by the writer in the year 1921 and culminating in the discovery of the effect of a change of frequency described in the lecture on "A New Radiation" in February 1928. The method of observation described in that lecture involves the use of monochromatic light and a spectroscope. To take a specific example, we allow the beam of light from a mercury arc lamp to pass through a crystal of diamond. Focussing an image of the illuminated diamond on the slit of a spectroscope, we observe in the light scattered in the substance of the diamond, new lines not present in the incident

radiation. Corresponding to each monochromatic line in the incident radiation, there is a second and additional line, the wave-number of which is less by 1332 per centimetre than for the incident light. A third and much feebler line of which the wave-number *exceeds* that of the incident light by 1332 per centimetre is also weakly recorded in the spectrum. Numerous such studies of the scattering of light in crystals have been made since they were first described. It is abundantly clear from the observations that they cannot be explained on the basis of the ideas of the classical wave-theory alone. It is necessary to introduce the concept of the photon or a quantum of radiation, the energy of which is proportional to the frequency of the corresponding waves. The change of frequency as actually observed appears on the quantum theory as due to an exchange of energy between the photon and the crystal, a diminution of frequency if the photon is the donor and the crystal the acceptor, and an increase if the reverse is the case.

The investigation of light scattering in crystals is a powerful method for the study of the solid state. But it is beset by peculiar experimental difficulties. Theory indicates that a perfectly homogeneous crystal would scatter no light at all; the diffusion of light theoretically possible is that due to the vibrations of the crystal lattice excited by the incident light and occurs in every case with a change of frequency. Unfortunately, however, actual crystals are far from being perfect. Internal flaws and surface imperfections result in a strong scattering of light with unaltered frequency. Theoretically this should not trouble us at all, but practically it does trouble us very much. The difficulty arises from the fact that the incident light is not truly monochromatic and usually contains additional components and some continuous spectrum. If the crystal is not clear, or if the spectrograph gives appreciable coma or scattered light of its own, there is not much hope of getting useful results. Truly monochromatic light sources, clear crystals of sufficient size with polished faces, and spectrographs of high optical perfection and illuminating power are needed for such work. When these requirements are satisfied, results of great interest and value are forthcoming.

To appreciate the significance of the results obtained in such studies, we must remember that a crystal is not a mere geometric array of atoms, molecules or ions in space, but is a coherent structure of such particles having identical properties which are held together by powerful forces, thereby forming a rigid solid. It is inappropriate to consider the observed results in terms of the vibrations of the individual ions, atoms or molecules in a crystal. For, it is obviously not possible for any one particle in a crystal to vibrate without setting all the other particles in resonant vibration. To understand the optical behaviour of a crystal rightly, we must consider it as a whole and set ourselves to discover the various modes of vibration of which its structure is capable. These vibrations divide themselves into two classes. In the first class of vibration, we can ignore the atomic architecture of the crystal and regard it as an elastic solid traversed by acoustic waves. The frequency of such vibration may be anything from zero upwards to a value so high that the corresponding wavelength becomes comparable with the

spacing of the atomic planes in the crystal. In the second class of vibration, we are dealing with movements which can only be understood or described in terms of the atomic architecture of the crystal. Such vibrations are referred to as the optical vibrations of the lattice. Some of these optical vibrations may have no counterpart at all for the substance in a fluid state and arise as a consequence of the crystal fields which bind the chemical units together into a rigid and ordered assemblage. Some of the optical vibrations, however, may have frequencies roughly corresponding to those characteristic of the ions or molecules in the fluid state. Even so, they cannot be identified with the vibrations of the individual chemical units. The optical vibrations—quite as much as the acoustic ones—are characteristic of the crystal structure and not of the individual particles present in the lattice cells.

The simplest way in which we may picture an optical vibration of a crystal lattice is to imagine the interpenetrating lattices of the simplest type present in the crystal, each carrying a single atom at the lattice points, to oscillate as rigid units relatively to each other, the centre of the inertia of the whole assembly remaining at rest. In such an oscillation, the crystal would throughout remain a homogeneous structure, but the relative positions of the atoms in its lattice cells would vary periodically with time. Such physical properties as the electric dipole moment, optical polarisabilities, and structure-amplitudes which determine the behaviour of radiation in various ranges of frequency in its passage through the crystal – would, therefore, also vary periodically with the frequency of the oscillation. It can be readily seen, however, that optical vibrations of the general description indicated would also be possible in which the phase of the oscillation changes slowly from place to place within the crystal. If this phase varies regularly in such manner as to repeat itself over a series of regularly spaced planes, the spacing of such planes is the phase wavelength of the optical vibration. An infinite phase-wavelength indicates a vibration identically the same throughout the crystal, and the optical frequency has then its limiting value.

The importance of the considerations set out above becomes clear when we consider the effect of radiations falling on a crystal. We may first refer to the case of a beam of infra-red radiation incident normally on the surface of a crystal. It is a well-known experimental fact that if the frequency of such radiation is within certain ranges characteristic of the particular substance, the radiations are powerfully reflected backwards by the crystal. This is the result of the optical vibrations of the crystal lattice being strongly excited by the incident waves. That such an excitation results in a directed reflection and not a diffuse scattering clearly indicates that the vibration of the crystal lattice is in the same phase at every point on the surface of the crystal. In the more general case of oblique incidence, in order that a regular geometric reflection may result, the excited lattice vibrations have necessarily to be coherent in phase, having everywhere the same relation to the phase of the resultant electric force due to the superposition of the incident and reflected waves. Since the waves necessarily penetrate to a

certain depth, it follows that such coherence in phase must extend also into the interior of the crystal.

Passing on to the case of the scattering of light within a crystal, it is evident that an optical vibration of the crystal lattice cannot be excited by the incident light if the phase of such vibration is the same throughout the volume of the crystal. This is evident from the principle of interference, as the effects of all the secondary radiations, irrespective of their frequency, would completely cancel out. In fact, it is easy to show that a scattering of light with altered frequency within a crystal would only be possible if the lattice-vibrations have phase waves which are equally inclined to the incident and scattered waves and so spaced that the scattering is in effect a monochromatic reflection by an optically stratified medium. A very similar situation also arises when we consider the scattering of light as the result of the acoustic vibrations of the crystal lattice. The usual formula for a monochromatic reflection connects the wavelength of the incident radiation, the spacing of the optical stratifications and the glancing angle which is half the angle of scattering. This formula which follows from the classical wave-principles has its counterpart in the quantum theory, appearing as a consequence of the conservation of energy and momentum in the collision between the photon and the acoustic or optical disturbance in the crystal.

Having considered the cases of infra-red radiation, and of ordinary light, we naturally pass over to the X-ray optics of crystals. It is fairly obvious that, as in the case of ordinary light, an acoustic vibration of the lattice can only give rise to a diffuse scattering of the X-rays. The position is entirely different in regard to the optical vibrations of the crystal lattice. It follows from the very nature of an optical vibration that it does not involve any variation in the mean electronic density of a unit cell in the lattice, but can cause only periodic variations of the structure-amplitudes of the crystal. In other words, the effect of an optical vibration is to cause a variation having its own frequency in the reflecting power of the regular crystal spacings. We may put this a little differently by stating that the optical vibration creates dynamic stratifications of electron density, and that these can give regular X-ray reflections but with a change of frequency, in much the same way as the static planes give the classical reflections without change of frequency. The spacing and orientation of the dynamic stratifications are identical with those of the static spacings when the phase-wavelength is infinite. More generally, these quantities and, therefore, also the geometric law of the modified reflection, would depend on the wavelength of the phase-waves and the angles which they make with the crystal spacings and with the plane of incidence. The geometric law of quantum X-ray reflection for the most general case has been deduced by Raman and Nath in a paper published in the *Proceedings* of the Academy for November 1940, and takes a quite simple form. It will suffice here to remark that the theory shows that the reflection should appear in precisely specifiable directions. In other words, *the spacings of a crystal should give, in addition to the classical or unmodified reflections, quantum or modified reflections*

obeying a different geometric law. It is no exaggeration to remark that this new result is of the greatest importance both to X-ray optics and to crystal physics. For the experimental proof of this thesis, it is necessary that sharply defined X-ray reflections of which the positions agree with those theoretically deduced should be found in association with every crystal plane of which the structure amplitude is sufficiently large and is strongly modulated by the possible vibrations of the lattice. That this is actually the case has been demonstrated in a series of communications published during the year by Raman and Nilakantan. A specially detailed investigation for the case of diamond is appearing shortly in the *Proceedings*, which brings out in a convincing way the physical reality of the phase-waves associated with the optical vibrations of the crystal lattice. The prediction made earlier in the year that the intensity of the modified reflections given by diamond should remain unaffected at liquid air temperatures has also been completely confirmed. *The quantum theoretical character of the new reflections has thus been completely established.*

Returning to the case of the scattering of ordinary light, it may be remarked that both the acoustic and optical vibrations of the crystal lattice reveal themselves in it. The vibrations of the latter class are usually subdivided into external and internal vibrations. Though this distinction is somewhat arbitrary, it is in many cases useful; and indeed, in relation to the crystal structure, the external vibrations, the frequency of which is determined by the crystal fields and are usually much lower, are even more important than the internal vibrations. The thermal behaviour of the external oscillations is particularly interesting. The very careful studies of the temperature effect which have been made by Nedungadi in the cases of sodium nitrate and of quartz have been very illuminating. Nedungadi's studies indicate that any transformation in crystalline form is usually *preceded* by notable changes in the magnitude and character of the low-frequency shifts. The changes observed in the case of α -quartz greatly assist in understanding the remarkable variations of physical properties which precede the α - β transformation of quartz.

The case of α -quartz has been very exhaustively investigated by Saksena with a view to identifying the various modes of optical vibrations appearing in the spectrum of the scattered light and correlating these with the known infra-red spectrum of α -quartz and with the specific heat of the crystal. The investigation must be considered to have been highly successful, as the theoretically predicted and experimentally observed behaviours show an almost complete agreement. The theoretical part of the investigation was based on an application of the methods of the group theory to the known structure of the crystal and the determination of its symmetry modes of vibration. The verification of the theoretical conclusions required an investigation of the spectra with the incident light polarised in different ways and with the crystal in different orientations, as also an analysis of the scattered light in each case. Such an investigation is naturally laborious and time-consuming, but the results in the case of quartz

appear fully to have justified the trouble taken. It is very satisfactory to find from the work of Bhagavantam with calcite, and of Saksena with quartz, that the theoretical selection rules for the appearance and non-appearance of certain vibrations in the spectra are found to be obeyed. These selection rules may be deduced geometrically from the known form of the optical polarisability ellipsoid of the crystal and the character of the deformations it should undergo for vibrations of the different possible types of symmetry. The fact that the results deduced are in accord with the experimental results shows clearly that we are dealing with the vibrations of the crystal lattice and not of the individual chemical units in it, as remarked earlier in this address.

Summary

The excitation of the optical modes of vibration of a crystal lattice by radiations incident on the crystal is discussed. The optical vibrations can be described as oscillations of the interpenetrating lattices in the crystal with respect to one another. They give rise to a periodic variation of the physical constants, e.g., electric dipole-moment, optical polarisabilities, structure amplitudes, which influence the behaviour of radiation in various ranges of frequency in its passage through the crystal. The phenomena observed in the different ranges of frequency have a common feature, namely that the incident radiation excites the crystal vibrations of which the phases are everywhere in coherent relationship with the phase of the radiation field. The scattering of light or the reflection of X-rays with change of frequency appears as the result of the phase of the lattice vibrations varying from point to point in such manner that the crystal is, in effect, an optically stratified medium giving a monochromatic reflection of the incident rays at the appropriate angle of incidence determined by the spacing of the stratifications and the wavelength of the incident radiation. The description of the observed effects in the language of the wave-theory and in terms of the quantum hypothesis are complementary and do not in any way contradict each other.

The paper includes a review of 14 communications dealing with this field of research published during the year 1940 in the *Proceedings of the Indian Academy of Sciences*.

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The quantum theory of X-ray reflection: basic ideas

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1. Introduction

The phenomena arising when a beam of X-rays traverses a crystal and ascribable to the possible or actual movements of the atoms in it from their positions of equilibrium are of very great interest, since their study may be expected to throw light on the nature of such atomic movements and also on the nature of the interaction between the X-rays and the material particles of the medium. In the analogous case of a beam of monochromatic light traversing a transparent crystal, the phenomenon of the scattering of light with change of frequency first observed by the present writer in 1928 renders a direct spectroscopic investigation of the atomic vibrations possible. Much light has been recently thrown on the subject of crystal physics by such spectroscopic studies. Indeed, the new knowledge derived in this way necessitates a radical revision of the ideas hitherto accepted concerning the dynamics of crystal lattices and the thermal energy of crystals. Further, the optical investigations show very clearly that the interchanges of energy and momentum between the radiation and the crystal lattice are determined by the principles of the quantum mechanics and not by the

classical ideas. Early last year (1940), it was observed by Dr P Nilakantan and the present writer that the (111) crystal planes of diamond exhibit monochromatic X-ray reflections of a new type which are as sharply defined as the ordinary or Laue reflections but which obey a wholly different geometric law. Further, the intensity of these reflections, though definitely smaller than the intensity of the classical X-ray reflections, is of the same order of magnitude and is not appreciably altered by either rise or fall of the temperature of the crystal. These and other observations of a fundamental character revealed the existence of a whole group of X-ray phenomena which lie outside the scope of the existing theoretical developments of the subject. It thus becomes necessary to re-examine the assumptions on which the existing theories are based and to build a new theoretical structure in better accord with facts.

2. The failure of the classical mechanics

In an essay on the molecular diffraction of light published in 1922, the present writer showed that, contrary to the opinion generally held at that time, transparent crystals such as quartz, rock-salt and ice traversed by a beam of light exhibit a true opalescence or diffusion of light associated with the ultimate structure of the crystal. This diffusion was provisionally attributed to the disordering of the crystal lattice by thermal agitation. The subsequent observation by the present writer that the spectrum of the light so scattered by crystals exhibits changes of frequency placed a new complexion on the matter. The incident light being monochromatic, frequency differences between the incident and scattered radiations are observed which fall in the infra-red region of the spectrum and are therefore to be identified with certain specific modes of vibration of the crystal structure. If the appearance of such vibrations in the spectrum of the scattered light had been due to thermal agitation in the crystal, it would follow from the principles of optics and electrodynamics that the radiations of *increased* and *diminished* frequencies should appear with *equal intensity*. Actually, this is very far from being the case. Indeed, when the frequency differences are large, we observe *only* scattered radiations with diminished and *none* of increased frequencies. These facts indicate that the vibrations of the crystal lattice revealed by the spectroscopist are produced or induced by the light itself. Further, quantitative studies of intensity show that this is the correct view of the matter even if such vibrations are of sufficiently low frequency to be appreciably excited by thermal agitation. The light induces a step-down or a further step-up of the vibration as the case may be, appearing as scattered light with increased and diminished frequencies respectively, though with greater intensity corresponding to the greater amplitude of vibration. The facts thus compel us to recognise that the observed scattering of light is in every case

associated with the changes in the energy level of vibration induced by the light itself.

The spectroscopic evidence thus makes it clear that the scattering of light in crystals is a quantum-mechanical effect, the exchanges of energy between the photons and the crystal lattice occurring in discrete units or quanta of vibrational energy. When these units of energy are sufficiently small, in other words when the frequencies of mechanical vibration of the crystal lattice are sufficiently low, the quantum-mechanical picture of the facts tends asymptotically towards the purely classical picture in which the scattered light should appear with equal intensity with increased and diminished frequencies. In other words, the quantum description has a classical analogue; the latter, however, bears no resemblance to the facts except when the vibrations of the crystal are of very low frequency or the temperature of the crystal is very high. The lower the temperature of the crystal, and the higher the frequency of a particular vibration, the less would the actual facts resemble the picture suggested by the classical ideas.

That the propagation of X-rays through a crystal is influenced by the atomic vibrations is shown by the diminishing intensity of the spots in a Laue pattern when the crystal is heated. Numerous physicists, amongst them Debye (1914), Brillouin (1922), Waller (1923, 1927), and Laue (1926), have considered this problem from a semi-classical point of view. Laue in his memoir of 1926 drew attention to a very important feature emerging from his treatment of the problem, namely that all secondary radiations from the crystal, except those appearing as the geometric reflections by the lattice planes, suffer a change of frequency. The origin of this change of frequency is readily understood. An atom occupying a fixed position in space would naturally emit secondary radiations having the same frequency as the primary X-ray falling upon it. An oscillation of the atom about its position of equilibrium would result in a periodic variation of phase of such secondary radiation. The analysis indicates that the secondary radiations would then include components with their frequency increased and diminished respectively by the oscillation frequency of the atom. These components appear with an intensity which rapidly increases with the amplitude of the atomic vibration, the intensity of the component of unmodified frequency diminishing *pari passu*. Laue emphasised that these changes of frequency play a fundamental rôle in determining the observed optical effects. For, only such radiations as have identically the same frequency can be coherent with each other; any difference of frequency however small would render coherence impossible. A frequency analysis of the secondary radiations and therefore also of the atomic vibrations is thus a necessary preliminary to a proper investigation of the problem.

Laue showed that the secondary radiations from the atoms in the crystal vibrating with a specified frequency yield a resultant in which the *components with increased and diminished frequency appear superposed with identical intensity*. The situation is thus exactly similar to that arising in the theory of the scattering of light in a crystal when considered classically, and it automatically follows that the

classical mechanics must also fail in the X-ray problem. The change over from classical to quantum mechanics is fortunately simple. The conservation of energy as between the X-ray quantum and the crystal is equivalent classically to a change of frequency of the radiation, such change, however, occurring in one direction or the other and not in both at once. The conservation of momentum in the encounter between the X-ray quantum and the crystal is equivalent classically to the usual formula for a monochromatic reflection of incident radiation by a stratified medium, the stratifications being now dynamic and not static. The correct intensity for the radiation of modified frequency resulting from the encounter is found by associating one energy quantum of the appropriate frequency with each degree of freedom of vibration of the crystal lattice. The effect of thermal agitation in the crystal enters into the quantum mechanical scheme for the X-ray problem in exactly the same way as in the parallel problem of the scattering of light.

3. The vibration spectrum of a crystal

Einstein who was the pioneer in the development of the quantum theory of specific heats suggested that the vibrations of the atoms in a solid have *monochromatic* frequencies and showed how these frequencies could be connected with the observed variation of specific heat with temperature. He also explained how in simple cases the order of magnitude of these frequencies could be inferred from the elastic properties of the solid. The alternative hypothesis put forward by Debye, namely that the frequencies of atomic vibration in a solid form a continuous spectrum which may be identified with its elastic vibrations, subsequently however found its way into general favour. The success of the Debye formula in representing the course of the specific heat curve in several cases promoted the belief that the hypothesis correctly represents the actual vibration spectrum of simple solids. That this belief is illusory becomes evident on a closer examination of the facts.

In the first place, it may be pointed out that while a knowledge of the vibration spectrum enables us uniquely to determine the specific heat curve, it can scarcely be suggested that a knowledge of the specific heat curve enables us uniquely to determine the vibration spectrum. Indeed, whenever it has been possible to make a direct spectroscopic study of the vibration spectrum of a solid, the claim of the Debye hypothesis to represent the same is shown to be false. Taking for instance the case of diamond, the studies of Bhagavantam (1930) on the scattering of light in this crystal, and the recent investigations of Nayar (1941) on its luminescence at low temperatures show the lattice spectrum of diamond to consist of numerous discrete or monochromatic frequencies, some of them being much smaller than the so-called limiting frequency calculated from the Debye formula. The spectrum of the scattering of light in sulphur and phosphorus similarly exhibits

numerous discrete lines, including some with very low frequency shifts, indicating that most of the degrees of freedom of atomic vibration are represented by monochromatic vibrations as originally pictured by Einstein. The position is equally striking when we consider crystals of apparently simple chemical composition, e.g., quartz. Mr Saksena (1940) has shown by a detailed investigation that no less than 24 out of every 27 degrees of freedom are represented in the vibration spectrum of this crystal by monochromatic frequencies.

It is known that the Debye formula fails to represent the specific heat curves correctly in several cases. It may be pointed out that these failures are actually more significant than the successes of the formula in other cases. Elaborate hypothesis have been put forward to explain away these failures, overlooking the simple explanation indicated by the spectroscopy, namely, that the vibration spectrum of every crystal, however simple in its chemical composition, includes several monochromatic frequencies. When these frequencies are known, the specific heat formula necessarily contains corresponding Einstein terms, and this involves a reduction (usually very drastic) in the number of degrees of freedom allotted to the Debye term, as also of its "limiting frequency". In the case of diamond, for example, it is shown in a forthcoming paper by Mr V B Anand that the specific heat data are perfectly expressed in this way by the spectroscopically observed frequencies, only one-eighth of the total number of degrees of freedom being included in a term of the Debye type. On the other hand, a Debye function alone even with an arbitrarily assumed "limiting frequency" shows large deviations from the observed specific heats. It may reasonably be inferred that in other cases, e.g., metallic silicon or grey tin, where the Debye formula altogether fails to represent the specific heat data, the cause of failure is the same, namely that the vibration spectrum includes several monochromatic frequencies.

Thus, both the spectroscopic and specific heat data show unmistakably that the Debye picture of the vibration spectrum of a solid bears no resemblance to the facts, except in the region where it is *prima facie* appropriate, namely in respect of the elastic solid vibrations of the lowest frequencies whose wavelength is large compared with the lattice spacings of the crystal. The maximum possible contribution which such vibrations can make to the specific heat of the solid can be found by treating the lattice cell in the crystal as a single unit and assigning it three degrees of freedom of translatory movement. All other degrees of freedom of movement are necessarily associated with monochromatic or Einstein frequencies of vibration of the crystal structure. Thus, in all crystals, including even those which are elementary or of the simplest chemical composition, the vibration spectrum is essentially of the type pictured by Einstein, and consists of discrete or monochromatic frequencies lying in the infra-red or high-frequency region. This is accompanied in the region of low frequencies by a continuous spectrum of elastic vibrations. The contribution of the latter to the thermal energy would be relatively of minor importance for the vast majority of crystals except at the lowest temperatures.

4. Character of the Einstein vibrations

We may now proceed to consider the nature of the monochromatic vibrations. It is evident that they arise from a periodic variation with time of the basic grouping of the atoms in the unit cells of the lattice. Such a vibration obviously cannot be confined to an individual cell, for its energy would then be rapidly passed on to the neighbouring cells and would be immediately damped out. We must, in fact, picture the vibrations as taking place simultaneously and in identically the same way in all the cells of the lattice. The frequency of such vibrations as well as their modes would be determined by the internal architecture of the crystal, in other words by the geometric grouping of the atoms and the forces which they exert on each other. If the number of the lattice cells be sufficiently large, as would be the case even for a sub-microscopic crystal, these frequencies and modes would be wholly independent of the size or shape of the crystal. The vibrations must, in the limiting case, be pictured as having an identical frequency, amplitude, and phase in all the cells of the lattice, as only then could the motion be truly monochromatic. Any variation in the phase of the vibration at different points in the crystal would involve a departure from perfect monochromatism, but this would be negligible provided the phase wavelength is sufficiently great to include a large number of lattice cells. Phase wavelengths comparable with the dimensions of the lattice cells would be altogether excluded, and in general the smaller wavelengths would be much less probable than the larger ones for which the frequency is independent of wavelength. The possible orientations of the phase waves would be determined by the geometry of the atomic grouping and especially by its symmetry characters.

Turning now to the continuous spectrum of elastic or low frequency vibrations, the situation here is totally different. The atomic structure of the solid does not enter into the picture. The possible frequencies of vibration are explicitly determined by the macroscopic dimensions of the crystal and their relation to the velocity of the wave propagation, the spectrum extending continually towards lower frequencies as the dimensions of the crystal are enlarged. The frequencies vary with the wavelengths, being inversely proportional to them. The possible wavelengths being determined by the dimensions of the crystal, it follows from simple geometry that the cases in which the wavelengths are small are much more numerous than those in which they are large. Further, the orientation of the wave-fronts is entirely arbitrary and bears no relation whatsoever to the symmetry characters of the crystal or its atomic architecture.

5. The fallacy of the Born postulate

As shown in the preceding pages, facts and principles alike compel us to reject the hypothesis of Debye as a description of the vibration spectrum of a crystalline solid except in the restricted region of low frequencies. We have also seen that

these low-frequency vibrations are altogether different in their character from the vibrations of higher frequency lying in the infra-red region of the spectrum. It follows that any treatment of the problems of crystal dynamics based on the concepts of Debye is necessarily fallacious. It may be remarked that the basic idea underlying Max Born's crystal dynamics is essentially the same as that of Debye, namely that all the possible vibrations of a crystal lattice are analogous to the elastic vibrations, having the same distribution of the phase-waves in respect of the wavelengths and their relation to the size of the crystal, as well as an identically similar distribution of the phase waves in respect of orientation in space. No proof or justification of this postulate seems ever to have been put forward. The so-called postulate of the "cyclic lattice" is in fact nothing more than an *ad hoc* hypothesis adopted for mathematical convenience. It is evident that this postulate is in total conflict with the conclusions at which we have arrived regarding the characters of the monochromatic vibrations of the crystal lattice. We shall therefore proceed to examine the Born postulate critically with reference to its claims to represent the actual state of affairs in a crystal.

One of the most remarkable facts brought into evidence by the study of the scattering of light in crystals is the extreme sharpness of the lines observed in the spectra of such scattering. Even in those few cases where the spectrum exhibits bands having an observable breadth, these sharpen to the finest lines when the crystal is cooled down to low temperatures. A perfect monochromatism of the vibrations of the lattice in the infra-red region is thus to be regarded as a characteristic property of the crystalline state, at least under ideal conditions. Not only is this true in respect of such vibrations as are also observable with the substance in the molten or dissolved condition, but it is equally so in respect of such vibrations as are specially characteristic of the crystalline state. It is obviously impossible to reconcile this situation with the idea that these vibrations are of the same nature as the elastic vibrations giving a continuous spectrum of frequencies.

To exhibit the fundamental error in Born's postulate, we may consider the behaviour of a model consisting of N Planck oscillators of identically the same kind regularly arranged in geometric order inside a box. The postulate of Born assumes that the dynamic behaviour of these oscillators could be represented by a three-dimensional Fourier series whose wavelengths are sub-multiples of the dimensions of the box and in which all the terms have equal weight. The assumption is, *prima facie*, unjustifiable because we are not here concerned with possible translatory movements of the oscillators which would involve collisions with the walls of the box, but only with the internal oscillations of the individual units in fixed positions. Accepting the postulate however for a moment, we may consider its implications in regard to the behaviour of the oscillators in our model. The essence of a Fourier representation is that the summation of the terms can reproduce the most arbitrary kind of disturbance. In the present case, since the series contains the full number of terms, namely N , all of which have equal

weight, it would mean that their superposition would result in the phases of the individual oscillators being entirely arbitrary and uncorrelated with each other. This is evidently a *reductio ad absurdum*, since such a state of affairs could only exist when the Planck oscillators are entirely independent of each other, as would be the case if we were considering the molecules of a gas. It is a fundamental aspect of the crystalline state that the oscillators of which it is composed are coupled to each other more or less firmly. In diamond, for example, the bonds connecting the different lattice cells with each other are exactly of the same kind as those which bind the atoms within the cell. The proposition that the internal oscillations occurring in the neighbouring cells of the lattice are uncorrelated in phase is thus entirely indefensible. Indeed, it would be more reasonable to make exactly the contrary assumption, namely that the phases of the oscillations in neighbouring cells are so highly correlated with each other that to all intents and purposes, the entire piece of diamond functions as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency. Only on some such view could we hope to understand the extraordinarily perfect monochromatism of the lattice vibrations in diamond.

We may summarise the situation by stating that the Born postulate does not represent the true state of affairs in a crystal except in regard to the low-frequency elastic vibrations, in which case, of course, it is of no particular significance. The real state of affairs in a crystal demands that if the distribution of phase of the Planck oscillators in a specified volume could be represented as a three-dimensional Fourier series, only the terms which have wavelengths large compared with the lattice spacings and orientations specifically related to the geometry of the crystal structure would be allowed, while terms with phase wavelengths of the same order as the lattice spacings would be altogether excluded. The stronger the atomic forces and the tighter the resultant mechanical coupling between the lattice cells, the more nearly would we approach a state of affairs in which the entire crystal behaves as a single oscillator with N times the statistical weight of a Planck oscillator of the same frequency.

6. Fundamental defects of the existing theories

Born's postulate of the cyclic lattice which has been discussed in the foregoing pages and shown to be untenable was the basis on which Debye, Waller and Laue developed their treatments of the problem of the temperature effect in X-ray diffraction. It follows that, quite apart from the incompetence of the classical mechanics to deal correctly with the problem, these earlier investigations were also otherwise fundamentally defective, being in fact based on an erroneous conception of the nature of the vibrations in a crystal lattice. The picture of the X-ray phenomena which they present differs radically from the truth, failing as it does to indicate the fundamental difference between the low-frequency or

continuous spectrum of elastic vibrations and the high-frequency or monochromatic vibrations in the infra-red, in respect of the X-ray effects to which they give rise. This is not surprising as the theories start from the assumption that these modes of vibration are essentially similar.

To make the foregoing points clear, we proceed to show from first principles how essentially the X-ray effects due to these two types of vibration of the lattice must differ. We shall consider first the elastic vibrations of the crystal lattice. These involve translatory movements of the lattice cells of the crystal from their positions of equilibrium. It is evident that if there are N lattice cells in the crystal, such translations would involve $3N$ degrees of freedom. They may therefore be regarded as due to the superposition of $3N$ sets of elastic waves of all the possible wavelengths and frequencies, these having equal weight. It follows that the movements of any individual cell resulting from such superposition would be uncorrelated with that of any other lattice cell in the crystal. Hence, the secondary radiations of modified frequency sent out from the individual cells would be incoherent. In other words, the elastic vibrations would result in a secondary radiation of which the aggregate intensity is proportional to the number of lattice cells and which is in the nature of a diffuse or scattered radiation. This argument is not invalidated by the fact that the oscillation of a *particular* frequency expressed by one of the terms in the Fourier representation has a specifiable phase-relation in respect of the different lattice cells. The contradiction disappears when we remember that the number of degrees of freedom allotted to a *particular* frequency in a continuous spectrum is only one out of the very large number N . Hence, in spite of the fact that an elastic vibration of a specified frequency may be considered to be a coherent type of oscillation, the effect of all such vibrations taken together is essentially an incoherent radiation or diffuse scattering of which the intensity is proportional to N the number of lattice cells and not to N^2 .

The position is entirely different when we consider the monochromatic vibrations of the lattice cells. The monochromatism implies that all the N degrees of freedom refer to a single mode of oscillation, which in the limiting case is pictured as having identically the same frequency, amplitude and phase in all the lattice cells of the crystal. The movements of the atoms within a cell results in secondary radiations from the atoms, and therefore also from the cells, possessing components of modified frequency. The identity of the oscillation in all the lattice cells ensures that these secondary radiations received at any external point have coherent phase-relationships. Hence, these are capable, exactly as in the case of the secondary radiations of unmodified frequency, of giving rise to interference effects. Indeed, it is clear that they would result in a *geometric reflection of the X-rays by the lattice planes of the crystal but with modified frequency*. In the limiting case when all the cells vibrate in identical phase, the direction in which this modified geometric reflection would appear is the same as that of unmodified reflection.

We thus see that the elastic vibrations of the solid and the infra-red vibrations of the lattice cells give rise to X-ray effects which are fundamentally different and which, in fact, portray in a geometric form the radically different spectroscopic characters of the two modes of vibration. The elastic vibrations give a diffuse scattering of the incident X-rays with an intensity proportional to N , the number of lattice cells, while the infra-red vibrations give geometric reflections of altered frequency of which the intensity (subject to the same limitations as in the case of the unmodified reflections) is proportional to N^2 . It will be noticed that these results are consequential on our rejection of the Born postulate. Had the latter been valid, both types of vibration would have given a diffuse scattering proportional to N , the number of lattice cells; this, in fact, is the result emerging from the investigations of Debye, Waller and Laue, except that the actual result due to the elastic vibrations appears exaggerated in their papers by the assignment to them of $3 p N$ degrees of freedom instead of $3 N$ the correct number, p being the number of atoms in the unit cell of the lattice. That the internal vibrations within the lattice cells are not considered at all is clear from Laue's memoir where the positions of the atoms within the unit cell are explicitly regarded as constants.

7. Quantum reflection of X-rays

The preceding discussion enables us to proceed further and give a quantitative picture of the geometric reflection of X-rays by the lattice planes of a crystal with altered frequency. We consider the individual cells of the crystal lattice as Planck oscillators of frequency ν^* , so that, when excited, the energy of each oscillator is $h\nu^*$. An oscillation with this energy would result in the atoms in the cell being set in vibration such that the sum total of their kinetic energies in passing through the position of equilibrium is equal to $h\nu^*$. We then write down the expressions for the secondary radiations of various frequencies from each of the atoms in the cell. These are then summed up in the usual way, taking the positions of the atoms into account, to find the structure factor of the lattice cell. *This is done separately for each of the different frequencies of secondary radiation.* If the frequency ν^* is sufficiently high in relation to the temperature of the crystal, in other words, if $h\nu^* \gg kT$, it is sufficient to consider only the component having the primary or unmodified frequency ν and the component with diminished frequency $(\nu - \nu^*)$. Assuming that the setting of the crystal is such that the Laue conditions are satisfied for a particular set of lattice planes, it would follow that the primary X-rays of frequency ν would then be reflected by these planes. Simultaneously, the modified radiations of frequency $(\nu - \nu^*)$ would also be reflected by the same planes and in the same direction, provided we assume that the phase of the vibration of frequency ν^* is the same for all the cells in the crystal. The intensity of the modified reflection of frequency $(\nu - \nu^*)$ would be determined by the dynamic

structure factor of the lattice cell, in exactly the same way that the intensity of the unmodified reflection of frequency ν is determined by the static structure factor.

It will be noticed that this argument assumes that each of the N cells of the lattice is excited with an energy $h\nu^*$. It might seem at first sight that this would involve the entire crystal abstracting an energy $Nh\nu^*$ from the energy $h\nu$ of the incident X-ray photon, which of course, is impossible, besides being inconsistent with the assumed frequency $(\nu - \nu^*)$ of the reflection. Actually, all that the argument assumes is that the crystal functions as a single oscillator of frequency ν^* but with a statistical weight N times greater than that of a single lattice cell. This of course is only possible when all the cells vibrate in identically the same way, as is actually assumed in the argument. The intensity of the reflection calculated in this way would be the maximum possible. It may be regarded as an estimate of intensity to be expected in the most favourable setting of the crystal, viz., when the Laue conditions are satisfied also for the unmodified reflection. It may be emphasized that the quantum reflection is the result of a transition of the crystal from the ground state to a higher energy level of vibration, the energy required for the transition being derived from the incident radiations themselves and not from the energy of the thermal agitation of the crystal. Indeed in the circumstances considered, namely when $h\nu^* \gg kT$, thermal agitation is non-existent and can therefore play no part in the phenomenon. It may be remarked also that the so-called zero point energy which finds a place in the earlier semi-classical investigations of the X-ray problem becomes irrelevant from our present point of view.

8. Quantum scattering of X-rays

We now proceed to consider the X-ray effects arising from the elastic or low-frequency vibrations of the crystal lattice. As already remarked, these vibrations displace the lattice cells as a whole from their positions of equilibrium. Considering an elastic vibration of a particular wavelength, we notice that the stratifications in the medium arising from it are of two distinct kinds. Firstly, the elastic wave may itself, if it be of the longitudinal type, be regarded as a periodic stratification of electron density in a medium which may otherwise be considered as uniform. This view of the matter is appropriate when we are concerned with stratifications with a spacing greater than the largest grating intervals in the crystal. Secondly, the elastic waves, more particularly those of the transverse type, disturb the regular arrangement of the lattice cells, so that the structure amplitudes of the crystal plane are diminished and, *per contra*, new dynamic stratifications are created due to the superposition of the elastic waves and the static crystal planes. This is the point of view developed in detail in Laue's memoir. The scattering of the X-rays by either of the processes indicated would necessarily involve a change of frequency. The scattering by the elastic waves

themselves would appear in directions making smaller angles with the primary X-ray beam (assumed to be monochromatic) than the scattering due to their combinations with the crystal spacings. The two effects together give the background or diffuse scattering of X-rays by the crystal.

Since the elastic vibrations are of relatively low frequency, the situation may be represented in the majority of such cases by the inequality $h\nu^* \ll kT$, ν^* being the frequency of elastic vibration. When this is the case, the results to be expected from the classical and quantum theories would be identical. In other words, the effects observed may be described as the result of each of the elastic modes of vibration possessing an energy kT , the scattered radiations appearing with equal intensity in the two frequencies ($\nu \pm \nu^*$). It must not be assumed, however, that a treatment on these lines would represent the facts of X-ray scattering in every case. Whenever the elastic frequency ν^* under consideration is high or the temperature T of the crystal is low so that $h\nu^* \gg kT$, the situation would be reversed. The intensity of X-ray scattering would then be the result of assigning an energy $h\nu^*$ to each vibration, and it follows that it would then be much greater than that given by the classical considerations. Since the energy is abstracted from the incident quantum, the scattered radiation would then appear only with diminished frequency ($\nu - \nu^*$). It is evident also that the semi-classical considerations based on the Planck specific heat formula and the existence of zero point energy of the kind which figure in the earlier X-ray investigations cannot describe the situation correctly and are therefore irrelevant.

9. Characters of the two effects

It is evident from the foregoing discussion that the effects arising respectively from the vibrations in the infra-red and the elastic ranges of frequency are entirely different. Numerous criteria present themselves which make it possible to distinguish the one from the other.

Firstly – The geometric distribution of the secondary X-radiations is widely different in the two cases, being a regular reflection of the incident X-rays by the lattice planes in one case and a diffuse scattering in the other. The influence of the setting of the crystal on the two phenomena is determined by considerations of a wholly distinct kind and should therefore also be quite different.

Secondly – The intensity in one case is proportional to N^2 , viz., the square of the number of effective lattice cells and in the other case to N . Variations of the thickness of the crystal plate and of the cross-section of the X-ray beam traversing it would therefore influence the two phenomena in entirely different ways.

Thirdly – The dynamic structure amplitudes for the quantum reflections are determined by the modes of atomic vibration and are not necessarily proportional to the static structure amplitudes. It is quite possible, for instance, that the dynamic structure amplitude for a particular set of crystal planes is zero while the

static structure amplitude for the same planes is finite, or vice versa. In other words, the intensities of the classical and quantum reflections by any given set of crystal planes are not necessarily proportional to each other. Such a situation cannot arise in the quantum scattering of the X-rays, as this is due to the simple translatory movements of the lattice cells.

Fourthly – Since the two phenomena arise from vibrations of the crystal lattice lying in widely different ranges of frequency, their intensity variations with temperature would be markedly different. In either case, a finite limiting intensity would be reached at low temperatures, but this would be far greater relatively to the intensity at ordinary temperatures for the infra-red vibrations than for the elastic ones.

Fifthly – The characters of the quantum reflections and their variation with physical conditions such as temperature should exhibit a close correlation with the spectroscopic behaviour of the substance in the infra-red region; the quantum scattering, on the other hand, should show a correlation with the elastic behaviour of the substance.

Sixthly – The changes of frequency, if directly observable, would naturally be much greater for the quantum reflections than for the quantum scattering.

10. Summary

The paper examines the views generally current at the present time regarding the nature of the vibrations possible in a crystal lattice which are based largely on the specific heat theory of Debye and the crystal dynamics of Max Born and his school. The latter has for its starting point the so-called postulate of the “cyclic lattice”. It is here shown that this postulate is an *ad hoc* supposition adopted for mathematical convenience and that, far from being justifiable, its consequences are definitely contradicted by the known spectroscopic behaviour of crystals and that it is also contrary to the dynamic behaviour which should be expected from a set of coupled Planck oscillators such as the lattice cells of a crystal constitute. It is also shown that the modes of vibration of the elastic type forming a continuous spectrum and the modes of vibration having discrete or monochromatic frequencies in the infra-red region have fundamentally different dynamic characters. Starting from the proposition established by Laue that the secondary X-radiation from an oscillating atom exhibits components of modified frequency, it is shown how the resultant effects of the secondary radiations of modified frequency due respectively to these two types of vibration can be evaluated. It is shown further that the infra-red vibrations result in geometric reflections by the lattice planes of the crystal but with altered frequency, their intensity (subject to the same limitations as for the classical reflections) being proportional to N^2 , that is, to the square of the number of lattice cells in the crystal. On the other hand, the elastic vibrations of low frequency give a diffuse scattering of the X-rays of which

the intensity is proportional to N . As both these effects involve changes of frequency, the classical mechanics is incompetent to describe them correctly, and has therefore to be replaced by quantum-mechanical considerations. It is shown how this can be done quantitatively. The temperature dependence of both these effects is discussed. Finally, numerous experimental criteria are presented distinguishing the two effects which should prevent them from being mistaken for each other.

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Quantum theory of X-ray reflection: mathematical formulation

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10. Summary

1. Introduction

As was pointed out by Laue (1926), the secondary radiations from the atoms in a crystal traversed by a monochromatic beam of X-rays suffer changes of frequency when the atoms oscillate about their positions of equilibrium. These changes of frequency play a fundamental rôle in determining the observed X-ray phenomena. For, the superposition of radiations which differ in frequency cannot give rise to observable interferences, while, on the other hand, secondary radiations of identical frequency are necessarily coherent and capable of interfering with each other even if the frequency differs from the primary X-ray frequency. Accordingly, if we fix our attention on a particular mode of vibration of the atoms in a crystal, the radiations of altered frequency arising therefrom can give rise to interference maxima in just the same way as the radiations from stationary atoms. It follows also, that if several vibrations co-exist in a crystal, each set of secondary radiations of different frequency thus arising would produce its own interference maxima independently of the others. If, further, the individual vibrations are of

infinitesimal amplitude, a considerable simplification becomes possible. For, then each vibration may be regarded as giving rise to its own secondary radiations and acting independently of all the others, provided its frequency is different from theirs. This statement, however, requires some qualification when the excursions of the atoms about their positions of equilibrium resulting from the totality of all the vibrations present have a finite amplitude. For, the total radiation amplitude of an atom is fixed and is equal to the superposed radiation amplitudes of various frequencies. Hence, the radiation amplitude due to any particular vibration frequency would naturally be less than it would be in the absence of all the others. It is evident also that as the atomic excursions increase, the strength of the secondary radiations of the original or primary X-ray frequency and of the interference maxima to which they give rise must progressively diminish, finally tending to zero.

The elastic or low-frequency modes of vibration have a continuous spectrum of frequencies and hence, as explained above, the optical effects of each vibration should be considered separately. Since the energy corresponding to a particular frequency is small and is further distributed over all the atoms in the crystal, the resulting atomic amplitudes are exceedingly small. Hence, the secondary radiations due to these separate vibrations are exceedingly weak, and since they are incoherent, their intensities and not their amplitudes should be added. In the final result, therefore, we have an effect which is inherently feeble and which can only become important when a large volume of the crystal is under consideration.

The position is different when we consider the effect of modes of vibration of the crystal which appear as monochromatic frequencies in its infra-red spectrum. Each such line in the spectrum represents N co-existent modes of vibration, where N is the number of the lattice cells in the crystal. In the ideal case when all the N modes are of identical frequency, it is evident that the secondary radiations of altered frequency due to these co-existing modes would all be coherent and must therefore be considered *together* and *not separately*. It is evident, therefore, that the vibrations of the infra-red type can give rise to effects of an altogether higher order of intensity than the elastic vibrations considered above. This result has already been deduced in an earlier paper from a consideration of the phase relations subsisting between the lattice cells in a crystal in an infra-red vibration. Its possibility, it may be remarked, is consequential on our rejection of the ideas of Debye and Born regarding the nature of the high frequency vibrations in a crystal lattice, and especially of the so-called postulate of the "cyclic lattice" due to Born which we have considered in detail and shown to be untenable.

It should be noted that the elastic and infra-red modes of vibration of a crystal also differ in other respects. In the former case, the basic grouping of the atoms in the lattice cells remains unaltered, while in the latter, it is to be regarded as essentially a variable. Then again, the wave-fronts of an elastic vibration may have any possible orientation within the crystal, while for the infra-red vibrations, there is *prima facie* no reason for assuming that this should be the case. It has also

to be remembered that the elastic vibrations are of lower frequency than the infra-red ones; this makes a considerable difference in considering the influence of thermal agitation in the two cases.

As already explained in the preceding paper, the recognition of the changes of frequency, the importance of which was first emphasised by Laue, leads us naturally to bring the X-ray problem within the scope of the quantum theory of radiation. It also makes the transition from the classical to the quantum mechanical considerations very simple. The changes of frequency indicated by the classical electrodynamics appear in the quantum theory as the result of exchanges of energy between the quantum and the crystal lattice. Similarly, the Laue conditions for a dynamic reflection are the same as those required for the conservation of momentum in the encounter between the quantum and the crystal. The principal difference between the classical and quantum points of view is in regard to the question of the absolute intensity of the secondary radiations and its dependence on temperature. Here, the quantum mechanical considerations replace such incorrect applications of the quantum theory to X-ray physics as are usually made by introducing the Planck factor and the zero point energy, neither of which is really relevant when considering the exchanges of energy between matter and radiation.

2. Secondary radiations from an oscillating atom

Under the influence of waves of unit amplitude, an atom emits secondary radiations which at a distance R from the origin of co-ordinates and in a direction making an angle 2ψ with the primary ray have the amplitude

$$f \sin \beta \cdot \frac{e^2}{mc^2} \cdot \frac{1}{R} \cos 2\pi \left(vt - \frac{R + 2D \sin \psi}{\lambda} \right), \quad (1)$$

where D is the perpendicular distance of the atom from a reference plane through the origin bisecting the angle between the primary and secondary rays, f is the atomic structure factor, and β the angle between the electric vector in the incident pencil and the diffracted ray. It is evident that this expression would remain invariable if the atom moves parallel to the reference plane but would alter periodically if it oscillates perpendicular to it.

Writing

$$D = d + \alpha \cos(2\pi\nu^*t + z) \quad (2)$$

the periodic part of (1) may be written as

$$\cos [2\pi\nu t - Z - \zeta \cos(2\pi\nu^*t + z)] \quad (3)$$

where

$$Z = \frac{2\pi(R + 2d \sin \psi)}{\lambda}, \quad \zeta = \frac{4\pi\alpha \sin \psi}{\lambda}. \quad (4)$$

The expression (3) may be expanded in a series of Bessel functions. Neglecting the functions of higher order than the first, it may be written as

$$J_0(\zeta) \cos(2\pi\nu t - Z) + J_1(\zeta) \sin[2\pi(\nu \pm \nu^*)t - Z \pm z]. \quad (5)$$

The three quantities Z , ζ and z appearing in (5) are all phase angles. Z is the phase of the secondary radiation from the atom when it is in the position of equilibrium, ζ the change of this phase produced by displacing the atom through a distance α in a direction normal to the reference plane, and z is the phase of the atomic vibration. Expression (5) indicates that the secondary radiation from the oscillating atom consists of three components whose amplitudes depend on the amplitude of the oscillation and which differ in frequency and phase. The first component has the frequency ν of the primary X-rays and its phase is determined solely by the equilibrium position of the atom. Its amplitude has however been diminished by the movement of the atom in the ratio $J_0(\zeta):1$. The second and third components have the same amplitude, namely $J_1(\zeta)$, but they differ in frequency and phase. The component $(\nu + \nu^*)$ has a phase angle $(Z - z)$, while the component $(\nu - \nu^*)$ has a phase angle $(Z + z)$. The secondary radiations of altered frequency thus increase in amplitude with increasing vigour of the atomic vibration, while their phases are determined jointly by the atomic positions and the phase of the atomic vibrations. The equality of the amplitudes of the components of increased and diminished frequency indicated by (5) is a typical consequence of the classical electrodynamics which will later be amended in the light of quantum mechanics.

3. Dynamic stratifications of density

We may now proceed to deduce the optical effect of all the atoms vibrating with the same frequency but with a phase which may be assumed to vary slowly from

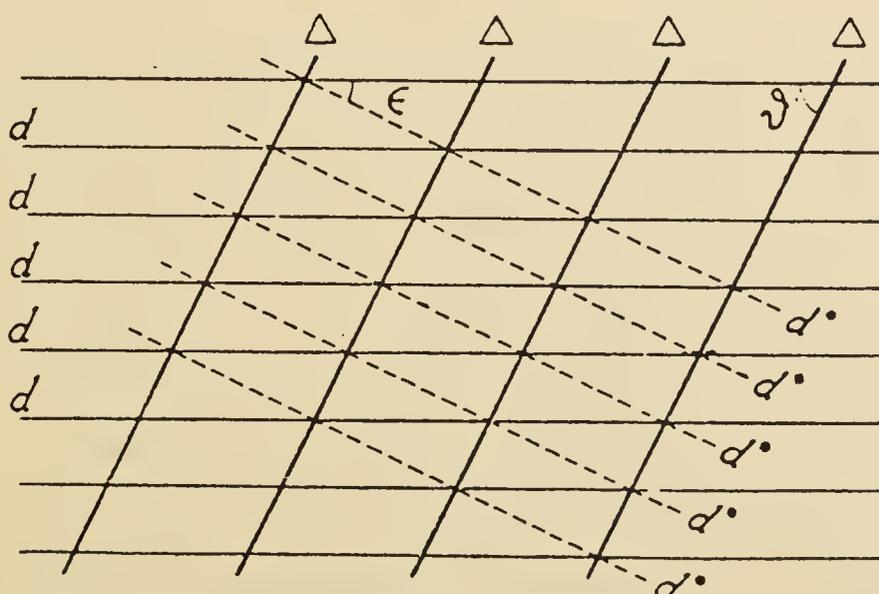


Figure 1. Graphical derivation of the dynamic spacings.

place to place within the crystal. For the purpose of a graphical derivation of the conditions for interference, it is not necessary at the present stage to distinguish between the elastic and infra-red modes of vibration. We consider a particular set of lattice planes in the crystal marked $d d d$ in figure 1.

It is evident that for any given setting of the crystal the phase of the secondary radiations as received at a distance will vary from point to point within the crystal. In respect of the secondary radiations of unmodified frequency, this phase is given by Z . Hence, to obtain the maximum resultant intensity, Z must be invariable along a crystal plane and jump by 2π or an integral multiple thereof, as we pass from plane to plane. In other words, the planes $d d d$ should make equal angles with the incident and diffracted rays, and their spacing d should satisfy the relation

$$2d \sin \theta_c = \lambda. \quad (6)$$

This is the familiar optical formula for a monochromatic reflection from a regularly stratified medium. θ_c indicates the glancing angle for a classical or unmodified reflection.

Considering now the secondary radiations of altered frequency, we see that their resultant is determined by the variation of $(Z - z)$ in one case and of $(Z + z)$ in the other. Let $\Delta \Delta \Delta$ in the figure represent the planes along which the phases of the atomic vibrations, in other words the values of z , are constant. In order to obtain the maximum intensity for the resultant of the secondary radiations, the crystal should be so set that $(Z - z)$ or $(Z + z)$ as the case may be, is constant along the lattice planes; it is evident from the figure that this would be the case if the setting of the crystal is such that the incident and diffracted rays are equally inclined to the planes which run diagonally cutting the $d d d$ and $\Delta \Delta \Delta$ planes, e.g., $/^*d^*d^*d^*$ as shown in figure 1. For obtaining the maximum intensity, a further condition must be satisfied, namely

$$2d^* \sin \psi = \lambda, \quad (7)$$

where ψ is, as before, half the angle between the incident and diffracted rays. It is evident from the figure that there are two sets of diagonal planes possible. But the same set will satisfy equation (7) for both the frequency components $(\nu + \nu^*)$ and $(\nu - \nu^*)$, provided that we assume the phase angle Z advances in one case and recedes in the other case as we move across the figure. The diagonal planes $d^*d^*d^*$ thus represent the dynamic stratifications of electronic density resulting from the vibrations of the atoms contained in the lattice planes of the crystal. As the phase waves $\Delta \Delta \Delta$ move from left to right, the dynamic stratifications $d^*d^*d^*$ move upwards, keeping a constant spacing, while if the phase waves $\Delta \Delta \Delta$ move from right to left, the spacings $d^*d^*d^*$ move downwards in the same way. The changes of frequency from ν to $(\nu \pm \nu^*)$ may thus be regarded as analogous to the Doppler effect in the reflection from a moving mirror.

4. Geometric law of dynamic reflection

The spacing d^* of the dynamic stratifications is connected with the spacing d of the static ones and the phase-wavelength Δ of the atomic vibrations by the vectorial relation,

$$\vec{1}d^* = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta}. \quad (8)$$

This is readily deduced by writing down the vectorial equation represented by the three sides of one of the triangles appearing in figure 1 and dividing the same by the area of the triangle. Denoting by ϑ the angle between the planes $d d d$ and the phase waves $\Delta \Delta \Delta$, and by ε the angle between the planes $d d d$ and $d^* d^* d^*$, we have from figure 1 and equation (8)

$$d^* \sin \vartheta = d \sin (\vartheta \pm \varepsilon) = \Delta \sin \varepsilon. \quad (9)$$

Substituting the first of these relations in (7), we obtain

$$2d \sin \psi \sin (\vartheta \pm \varepsilon) = \lambda \sin \vartheta. \quad (10)$$

Equation (10) is the general geometric law of dynamic reflection deduced by Raman and Nath (1940). It will be noticed from (9) that when the phase wavelength Δ is infinite, $\varepsilon = 0$ and $d^* = d$, from which it follows that $\psi = \theta_c$. In other words, the static and dynamic reflections then coincide in direction. This is also obvious directly from figure 1. In general, however, d^* and d are different, and the conditions for the possibility of static and dynamic reflections are not the same. While a static reflection can only occur at the particular setting of the crystal indicated by (6), a dynamic reflection is evidently possible over a wide range of settings of the crystal determined by the permissible values of the phase wavelength Δ . It is further to be remarked that while the glancing angles of incidence and reflection are equal for the static reflections given by (6), these angles when measured as usual with reference to the static crystal planes would generally differ from each other for the dynamic reflections. Further, the latter reflections would in general appear in a plane different from that of the incidence of the X-rays on the crystal spacings. To specify the actual plane of dynamic reflection, it is necessary to know the angle χ which determines the azimuth of the phase waves. We may put $\chi = 0$ in the case when the dynamic reflection appears in the plane of incidence, the phase waves then being evidently perpendicular to that plane. When $\chi \neq 0$, the dynamic reflection swings out of the plane of incidence to an extent determined by the values of Δ , ϑ and χ .

In the particular case when $\chi = 0$, it is evident that

$$\phi + \theta = 2\psi, \quad \text{and that} \quad \phi - \theta = 2\varepsilon, \quad (11)$$

where θ and ϕ are respectively the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Equation (10) may then be

written as

$$2d \sin \frac{\theta + \phi}{2} \sin \left(\vartheta \pm \frac{\theta - \phi}{2} \right) = \lambda \sin \phi. \quad (12)$$

The value of ϕ then depends on the angle ϑ . If we imagine ϑ to march from 0 to π , equation (12) shows that the relation between ϕ and θ will alter from

$$\phi = \theta, \quad \text{when } \vartheta = 0 \quad \text{or} \quad \pi \quad (13)$$

to

$$d(\sin \theta + \sin \phi) = \lambda, \quad \text{when } \vartheta = \frac{\pi}{2}. \quad (14)$$

Thus, when the phase waves are *parallel* to the crystal planes, the dynamic reflection always satisfies the ordinary geometric law of reflection from the crystal planes, while if the phase waves are transverse to the crystal planes, it appears in the direction given by (14) which may be written *approximately* as

$$2d \sin \frac{\theta + \phi}{2} = \lambda, \quad (15)$$

thereby indicating that the angle between the incident and reflected rays is approximately constant and independent of the crystal setting.

5. Dynamic structure factor

To find the conjoint effect of the secondary radiations from all the atoms in the unit cell of the lattice, we have to sum them up considering each component of frequency separately. This summation for the radiations having the primary X-ray frequency gives (omitting constant factors),

$$\sum_p j_p J_0(\zeta_p) \cos(2\pi\nu t - Z_p). \quad (16)$$

The summation for the secondary radiations of frequency $(\nu \pm \nu^*)$ similarly gives

$$\sum_p j'_p J_1(\zeta'_p) \sin [2\pi(\nu \pm \nu^*)t - Z'_p \pm z'_p] \quad (17)$$

the index p referring to the p th atom in the cell, and the dashes in (17) indicating that the setting of the crystal and the angle of diffraction are not necessarily the same as those considered in (16). Remembering, however, the conditions for a dynamic reflection discussed in the foregoing section, namely that $Z \pm z$ should be constant along any particular lattice plane, we may simplify (17) and write it in the form

$$\sum_p j'_p J_1(\zeta'_p) \sin [2\pi(\nu \pm \nu^*)t - Z_p], \quad (18)$$

Z_p having now the same significance as in (16) for a static reflection by the same set of lattice planes. A further simplification arises when the angle between the primary and diffracted radiations does not differ greatly for (16) and (18). We may then write, approximately, $j'_p = f_p$. If, further, the setting of the crystal in the two cases is not so greatly different, we may also write, $\zeta'_p = \zeta_p$, as an approximation. Subject to the restrictions indicated, (17) now takes the form

$$\sum_p f_p J_1(\zeta_p) \cdot \sin [2\pi(v \pm v^*)t - Z_p]. \quad (19)$$

The static structure factor of the unit cell as influenced by the particular vibration may therefore be evaluated by diminishing the structure factor of each atom in the ratio $J_0(\zeta_p)$ to unity. At the same time, the lattice cell acquires a dynamic structure factor which is found in exactly the same way except that the structure factor of each atom is now multiplied by $J_1(\zeta_p)$.

Very significant differences now arise in considering respectively the elastic and the infra-red vibrations. For the elastic vibrations, ζ_p is the same for all the atoms in the unit cell. The suffix p may therefore be removed and the Bessel functions taken outside the summation sign. For an elastic vibration, therefore, the static and dynamic reflections may be evaluated from the expressions

$$J_0(\zeta) \cdot \sum_p f_p \cdot \cos(2\pi vt - Z_p), \quad (20)$$

$$J_1(\zeta) \cdot \sum_p f_p \cdot \sin [2\pi(v \pm v^*)t - Z_p]. \quad (21)$$

The static and dynamic structure factors in the case of an elastic vibration thus differ only by a multiplying factor which is the same for all the atoms in the unit cell. Thus, if a particular set of crystal planes gives zero intensity for a particular order of reflection, the dynamic reflections for the same planes and the same order of reflection must also vanish. The dynamic reflections by different sets of crystal planes would follow the same order of intensity as the static reflections by those planes, provided the amplitude of the elastic vibrations transverse to the planes may be assumed to be the same. A similar remark would also apply to the relative intensities of the successive orders of reflection by a particular set of planes, except that the factor $J_0(\zeta)$ diminishes while the factor $J_1(\zeta)$ increases as the angle of diffraction becomes larger, *vide* equation (4).

The position is greatly altered when we consider the infra-red vibrations of the lattice. Here, the displacements being different for the different atoms, the factors $J_0(\zeta_p)$ and $J_1(\zeta_p)$ must remain within the summation signs. Some of the atoms in the lattice cell must evidently move in directions opposite to the others if the centre of gravity of the cell is to remain undisplaced. Hence $J_1(\zeta_p)$ would be positive for some of the atoms and negative for the others in an infra-red vibration, while on the other hand $J_0(\zeta_p)$ would always be positive and nearly equal to unity. It follows that the static and dynamic structure factors for an infra-

red vibration are determined by quite different considerations and cannot, in general, exhibit the close parallelism indicated by the theory for the elastic vibrations. Indeed, it may well happen that in particular cases, the static structure factor vanishes while the dynamic structure factor remains finite, or vice versa.

6. Quantum scattering by elastic vibrations

The disturbance produced by an elastic vibration on X-ray propagation is of two kinds. Firstly, a compressional wave would evidently alter the average electronic density. It is thus itself a dynamic stratification of the medium capable of reflecting the X-rays with a frequency ($\nu \pm \nu^*$), increased or decreased as the case may be, depending on the direction of the wave. Such a reflection occurs when

$$2\Delta \sin \psi = \lambda, \quad (22)$$

large values of Δ corresponding to small values of ψ , and vice versa. Thus, since Δ may have any one of a practically continuous series of values determined by the dimensions of the crystal, and since the orientation of the wave is arbitrary, the reflection indicated by equation (22) would result in a cone of scattered X-rays (the Brillouin cone) having the direction of the primary beam as its axis. The angular extension of the cone depends on the smallest permissible values of Δ . The intensity of such scattering would depend on the energy of the vibration and the resulting variation of electron density. On the classical mechanics, the energy of an elastic vibration of thermal origin may be taken as KT , while if the wave is quantum-mechanically excited by the incident radiation, the energy would be $h\nu^*$. The latter assumption would be the appropriate one to make if $h\nu^* \gg KT$, while if $h\nu^* \ll KT$, the former assumption would be correct. This type of X-ray scattering should therefore be exhibited by crystals even at the lowest temperatures and in the absence of thermal agitation, and especially by crystals of high elasticity, e.g., diamond. We should expect the intensity of the X-ray scattering by such crystals to be greater than that indicated by the classical considerations even at ordinary temperatures.

The second kind of disturbance to X-ray propagation arises from the distortions which the elastic waves cause to the regular stratifications of the crystal structure. The formulae of the three preceding sections enable us to evaluate these effects quantitatively in a very simple manner. As explained in section 3 and illustrated in figure 1, the superposition of an elastic vibration on a specified set of crystal planes gives rise to dynamic stratifications of density. As further explained in section 4, these stratifications reflect the incident X-rays in the direction given by the general geometric law (10). The intensity of such reflection is determined by the dynamic structure factor as explained in section 5.

Considering the *direction* in which the so-called dynamic reflection appears, it is evident from equations (9) and (10) that this depends on the wavelength Δ , the

angle ϑ which the wave-fronts make with the crystal spacings, and also upon the azimuth χ of the wave-fronts. A variation of χ would throw the dynamic reflection out of the plane of incidence, while if $\chi = 0$, the reflection would appear in that plane. A dynamic reflection is only possible when the X-ray wavelength, the dynamic spacing d^* and the glancing angle ψ of incidence of the X-rays thereon are suitably related. But since we have at our disposal two variables, namely Δ and ϑ , we may, as is evident from figure 1, by suitably altering both of them get a dynamic reflection *in any desired direction*. In other words, the resultant effect of all the elastic vibrations is a diffuse scattering of the X-rays over a wide range of solid angles and not a geometric reflection in any specified direction.

To find the X-ray scattering due to any particular set of crystal planes, we have only to evaluate the two expressions (20) and (21) given previously. Their magnitudes are in the ratio $J_0(\xi):J_1(\zeta)$. If ζ be sufficiently small, $J_0(\zeta)$ is practically unity while $J_1(\zeta)$ would be equal to $\frac{1}{2}\zeta$. If m be the mass of an unit cell of the lattice, the energy of vibration of N such cells, each having an amplitude α with a frequency ν^* would be $2\pi^2 m N \alpha^2 \nu^{*2}$. This may be written in the form $2\pi^2 \cdot M \sigma^2 \cdot \alpha^2 / \Delta^2$, where M is the mass of the whole crystal, σ is the velocity of the elastic waves and Δ is their wavelength. Utilising equations (4), (7) and (9), we may write this in the simple form

$$\frac{1}{2}\zeta^2 \cdot M \sigma^2 \cdot \sin^2 \varepsilon / \sin^2 \vartheta. \quad (23)$$

This may now be put equal to KT (classical mechanics). Accordingly, we have

$$\frac{1}{2}\zeta^2 = KT / M \sigma^2 \cdot \sin^2 \vartheta / \sin^2 \varepsilon. \quad (24)$$

Equation (24) gives the ratio of the sum of the squares of the dynamic structure factors to the square of the static structure factor. It is evidently of the order $1/N$ and is thus an exceedingly small quantity. The X-ray scattering in any specified direction due to the distortion of the crystal planes by the elastic waves is therefore of vanishingly small intensity in comparison with the intensity of regular reflection by the same crystal planes and should be unobservable except when relatively large volumes of the crystal are under consideration.

The numerical factor $\sin^2 \vartheta / \sin^2 \varepsilon$ appearing in equation (24) determines the manner in which the intensity of the scattered radiation varies with direction. It may be written also as Δ^2 / d^{*2} , where Δ and d^* have the same significance as in equation (8). Thus the intensity of the scattering would be greatest in those directions for which the wavelength Δ of the elastic waves which effectively scatter the X-rays is greatest. This variation arises because the amplitude of the elastic waves is directly proportional to their wavelength, and the scattering is therefore greatest in the directions in which the waves of longest wavelength and lowest frequency are effective. The nature of the variation can be readily made out from figure 2, which represents the geometric relation between $1/d$, $1/d^*$ and $1/\Delta$ given by equation (8), as also the relation between $1/d^*$, $1/\lambda$ and $\sin \psi$ expressed by equation (7).

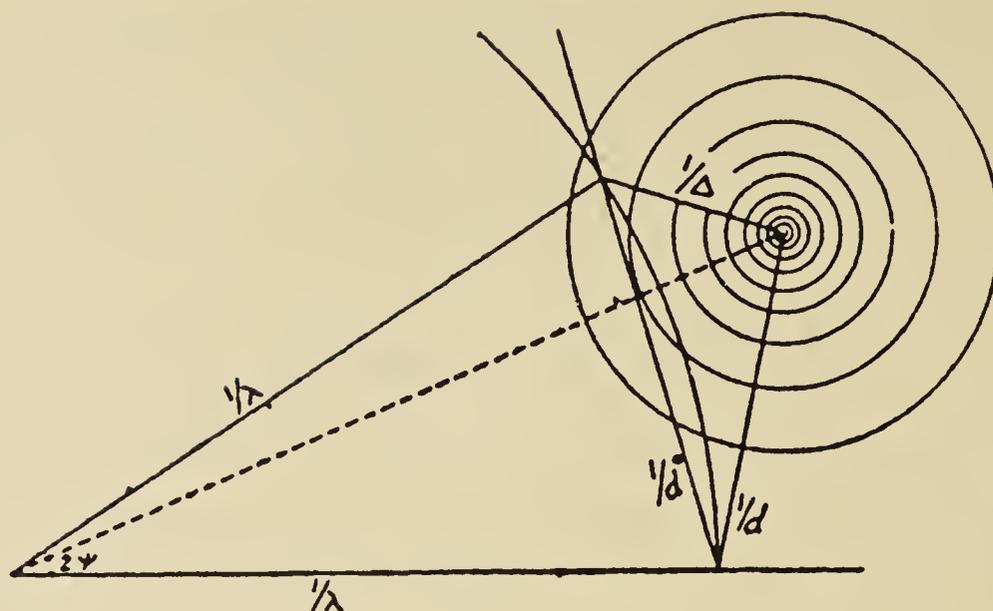


Figure 2. Distribution of intensity of diffuse X-ray scattering.

Spheres are drawn (sections of which by the plane of the figure appear as circles) round the terminus of the vector $1/d$ and with radii $1/\Delta$; points on the spheres represent various values and orientations of the vector $1/\Delta$ drawn from their common centre. The spheres are drawn closely together near their centre and further away at a distance from it to suggest the rapid diminution of the amplitude of the elastic waves with diminishing wavelength. A sphere of reflection is drawn with radius $1/\lambda$ around O as centre. It cuts across the "spheres of diffusion" having the radii $1/\Delta$ and the scattered radiations would therefore appear over the entire area of the sphere of reflection thus cut by the spheres of diffusion. When the sphere of reflection actually passes through the terminus of the vector $1/d$, the maximum of scattering intensity would fall on the sphere itself, but as it would then coincide with the regular reflection, the maximum would be unobservable. In other cases, the scattering would show a very broad and diffuse maximum of intensity corresponding to the minimum value of $1/\Delta$ on the sphere of reflection. This maximum however becomes rapidly weaker and more diffuse as the sphere of reflection passes further away from the centre of the spheres of diffusion with altered settings of the vector $1/d$. Hence, *nothing even remotely resembling a regular geometric reflection which persists over a wide range of settings of the crystal would be exhibited by the X-ray scattering due to the elastic waves.*

The same situation can be represented graphically by plotting the function $\sin^2 \vartheta / \sin^2 \varepsilon$ for various settings of the crystal. It is sufficient if this is done for the scattered radiations lying in the plane of incidence. With the aid of the formulae (6), (7), (9) and (11), it is readily shown that

$$\frac{\sin^2 \vartheta}{\sin^2 \varepsilon} = \frac{\sin^2 (\theta + \varepsilon)}{\sin^2 \theta_c - 2 \sin \theta_c \sin (\theta + \varepsilon) \cos \varepsilon + \sin^2 (\theta + \varepsilon)} \quad (25)$$

It is seen on differentiating the denominator of the expression on the right-hand side of (25) that it becomes a minimum and the whole expression is therefore a

maximum when

$$d \sin(\theta + \phi) = \lambda \cos \phi. \quad (26)$$

Equation (26) is equivalent to saying that $1/\Delta$ is then a minimum, as can be seen directly from figure 2. The values of $\sin^2 \vartheta / \sin^2 \varepsilon$ have been plotted in figure 3, as

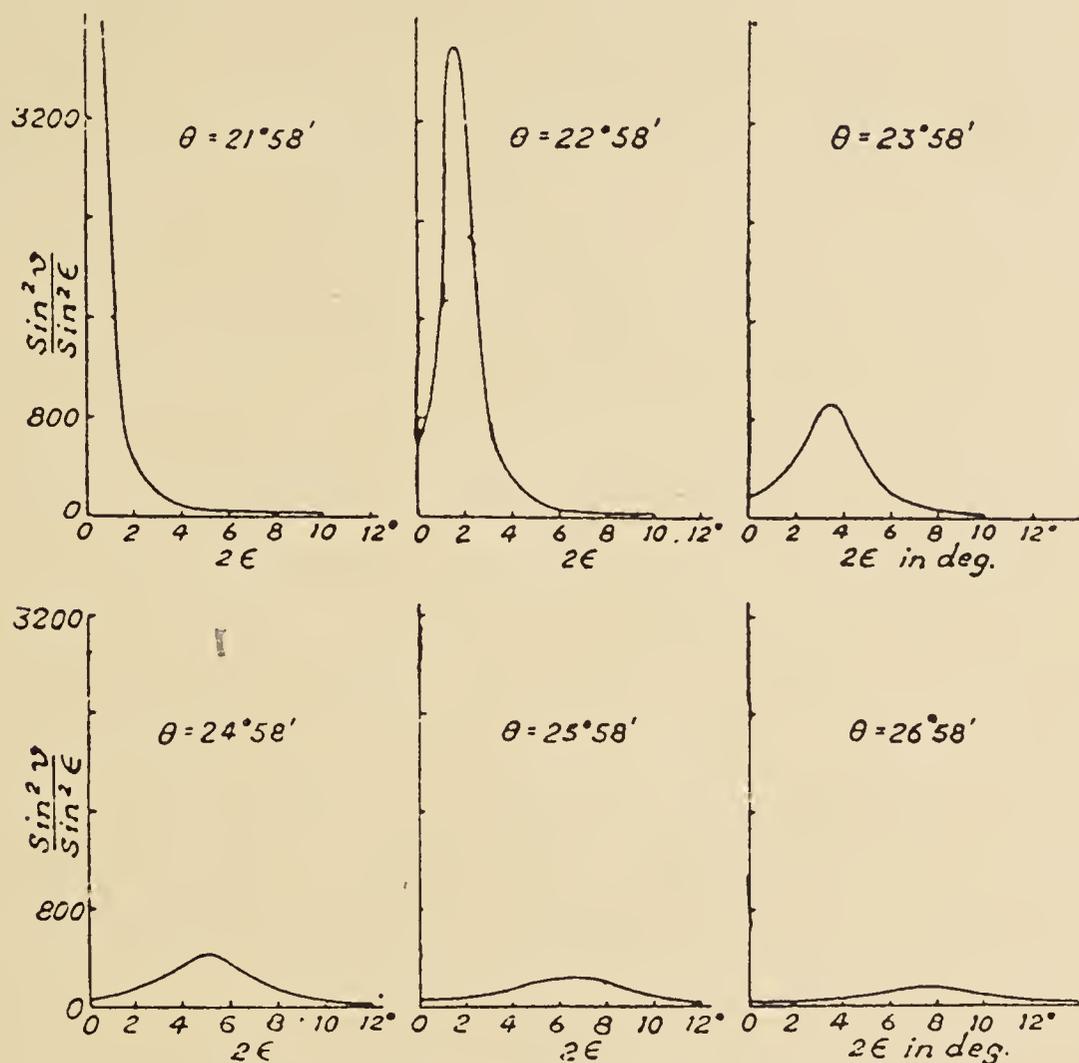


Figure 3. Graph of the function $\sin^2 \vartheta / \sin^2 \varepsilon$.

functions of the angle 2ε for six settings of the crystal indicated by the different glancing angles of incidence θ entered in the figures. The particular case chosen is one in which $\theta_c = 21^\circ 58'$; in the first of the six settings, θ has the value θ_c , and in the others increases by successive steps of one degree. It will be seen that the peak of intensity which appears in the first setting coinciding with the classical reflection rapidly falls off and is replaced by a relatively weak hump in the curve which spreads over many degrees of arc. The actual value of the numerical factor $\sin^2 \vartheta / \sin^2 \varepsilon$ also falls off rapidly and becomes insignificant as the crystal is turned away from the correct setting for a classical reflection.

We have in the foregoing analysis tacitly made certain simplifying assumptions, viz., that there is only one kind of elastic waves to be considered, that the velocity of the waves is a constant and that the atomic displacements due to the waves are in every case normal to the crystal planes. In reality, there are three sets of elastic waves possible, their velocity is a function of the direction of travel of the

waves, and the directions of the displacement are different for the three sets of waves. It should be remembered, however, that the three sets of waves would not all be equally effective in varying the structure amplitudes of the lattice planes. A movement of the atoms parallel to the lattice planes would have no X-ray effect and we may therefore exclude from consideration the types of waves which give rise to such displacements. Further, only such waves as have their wave-fronts roughly transverse to the lattice planes would produce a scattering of X-rays in directions which are appreciably displaced from the static reflections, and are therefore within the range of observation. It follows that we are principally concerned with distortional waves travelling in directions nearly parallel to the lattice planes under consideration and giving atomic displacements nearly normal to them. Hence, the simplified treatment we have adopted should be a fair approximation to the truth. The variation of the velocity of the elastic waves with the direction of travel may be readily taken account of in our formulae. In any event, such corrections as may be necessary would not affect the broad result which emerges from the theory, namely that the elastic waves produce only a diffuse scattering of the X-rays with very low intensity and not a geometric reflection of the X-rays in any particular direction.

It may be emphasized that the humps of intensity in the X-ray scattering curves appearing in figure 3 correspond to the elastic waves of greatest wavelength or lowest frequency operative in such scattering. Indeed, the smaller the angle at which the hump or maximum appears, and the more pronounced it therefore is, the lower would be the frequency of the elastic waves responsible for it. Accordingly, it is sufficient, as we have done, to take the energy of the individual vibrations as KT and to treat the problem classically. *At low temperatures, therefore, these maxima of scattering intensity should weaken still further and become altogether negligible. This should be so even for crystals of high elasticity, such as diamond, so long as we are considering the X-ray effects due to the elastic vibrations of lowest frequency for which $h\nu^* < KT$.*

7. Quantum reflection by infra-red vibrations

The geometric law of dynamic reflection (10) indicates that when the X-rays are incident on the lattice planes at an appropriate angle, the static and dynamic reflections appear simultaneously and in the same direction. The length of the phase waves Δ of the lattice vibration is then infinite, in other words, the atomic vibrations have everywhere the same phase. To enable us to evaluate the dynamic structure factor, we require to know the geometry of the particular mode of vibration as well as its actual amplitude. The former may be derived from a knowledge of the crystal structure and atomic forces, while the latter is determined by the energy of the vibration. The entire crystal being regarded as a single dynamic unit, the energy associated with a single non-degenerate mode of

its vibration would be KT on the basis of classical mechanics or $h\nu^*$ according to quantum mechanics. In considering the infra-red or monochromatic vibrations, however, the crystal must be considered as a system having a great number of identical or nearly identical frequencies. To obtain an idea of the results to be expected in consequence of this fact, we may make the simplifying assumption that all the N frequencies of the system are identical, N being the number of lattice cells in the crystal. It follows that the amplitude of the N modes of vibration should be superposed. Each *cell* in the lattice would then have energy KT (classical mechanics) or $h\nu^*$ (quantum mechanics). The resulting amplitudes of vibrations would be considerable and the dynamic structure factor would no longer be negligibly small in comparison with the static structure factor. Considering also the identity of the phase of the vibration in the N cells, it follows that it would result in a dynamic X-ray reflection having an intensity proportional to N^2 and comparable with the intensity of the usual static reflections. In the language of quantum mechanics, we may express this by saying that the crystal takes up an energy of vibration $h\nu^*$ from the X-ray photon $h\nu$ which is reflected by the lattice planes with diminished energy $h(\nu - \nu^*)$, but that the probability of such a process occurring is increased N -fold by the fact that all the N cells co-operate, their frequencies, amplitudes and phases of vibration being identical.

On the basis of these ideas, we may evaluate the structure factor for a dynamic reflection when it appears in the same direction as a possible static reflection. Denoting by m_p the mass of the p th atom in the unit cell and by ξ_p its displacement from the position of equilibrium, the energy of a vibration of frequency ν^* may be written as

$$\sum_p 2m_p \xi_p^2 \pi^2 \nu^{*2} = h\nu^*. \quad (27)$$

From this we have

$$\sum \frac{1}{2} m_p \xi_p^2 = \frac{h}{4\pi^2 \nu^*}. \quad (28)$$

If the geometry of the vibration is known, we may evaluate the ξ_p 's from (28). Resolving each ξ_p in a direction normal to the chosen crystal planes, we obtain its component α_p and thence also ζ_p which appears in the dynamic structure factor. The latter may thus be determined for any particular mode of vibration and for the particular set of crystal planes. A similar procedure would have to be followed if we wish to consider any other possible mode of infra-red vibration or any other set of lattice planes. Taking $h = 6.55 \times 10^{-27}$ erg sec and with $m_p = 40 \times 10^{-24}$ gm and $\nu^* = 6 \times 10^{12}$ sec⁻¹ as representative values, the quantity $\sqrt{h/4\pi^2 m_p \nu^*}$ comes out as a length of the order 0.1 A.U. The ratio of $J_1(\zeta_p)$ and $J_0(\zeta_p)$ appearing respectively in the expressions for the dynamic and static factor is then of the order 1:20 for an average crystal. *In other words, under the most*

favourable conditions, the quantum or modified reflections have intensities which are of the same order of magnitude as the classical or unmodified reflections though, as a rule, definitely weaker.

It is worthy of remark that if a crystal has several possible infra-red modes of vibration, those of the lowest frequencies would in general, as indicated by (28), produce the most important X-ray effects. The special importance of the modes of lower frequency would however be less marked on the quantum theory than on the classical mechanics; this becomes evident on writing KT instead of $h\nu^*$ on the right-hand side of (27). We would then have ν^{*2} instead of ν^* in the denominator of (28). The question as to which of the possible infra-red modes is most effective is, however, not so summarily to be disposed of. Actually, each set of crystal planes would have to be considered separately in relation to the various possible modes of vibration in the lattice. It may well happen that the dynamic structure amplitude of a particular set of crystal planes is largely derived from one of the possible modes of vibration, while another set of planes is chiefly influenced by some other mode. It may also well happen that the dynamic structure factors determined by the aggregate effect of all the possible modes of vibration are widely different for different sets of crystal planes and bear no simple relation to the static structure factors of the same planes. Such special features would be characteristic of the individual crystal structure and of the particular modes of its infra-red vibration.

The simplifying assumption made above that all the N modes of vibration of the lattice have an identical frequency is equivalent to stating that the only possible phase wavelength is the largest possible, viz., $\Delta = \infty$. This is evidently an extreme assumption, and it would be more reasonable to expect that while the great majority of the possible modes of vibration correspond to a very great phase wavelength, the remainder correspond to lesser values of Δ , thus enabling the dynamic reflections to appear at other settings of the crystal as indicated by equation (10). It would then follow that the intensity of the dynamic reflections should diminish rapidly as the crystal is moved away from the setting at which the static and dynamic reflections appear superposed. The fall in intensity would, in fact, represent the distribution of the possible modes of vibration in respect of phase wavelength.

The situation indicated above is indicated graphically in figure 4. The reciprocal of the phase wavelength, namely $1/\Delta$, which we may denote by δ is represented as a vector drawn from the terminus of the vector $1/d$ which gives the spacing and setting of the crystal planes. The great majority of the possible values of δ congregate at the origin $\delta = 0$. There are, however, some which spread out along the lines representing the permitted directions of the phase-wave normal. The quantum reflections would then appear at the point or points on the sphere of reflection at which the vectors δ thus drawn meet the latter. As already explained, the dynamic reflections need not necessarily lie in the plane of incidence. The restriction of the vector δ to fall in specific directions differentiates our present

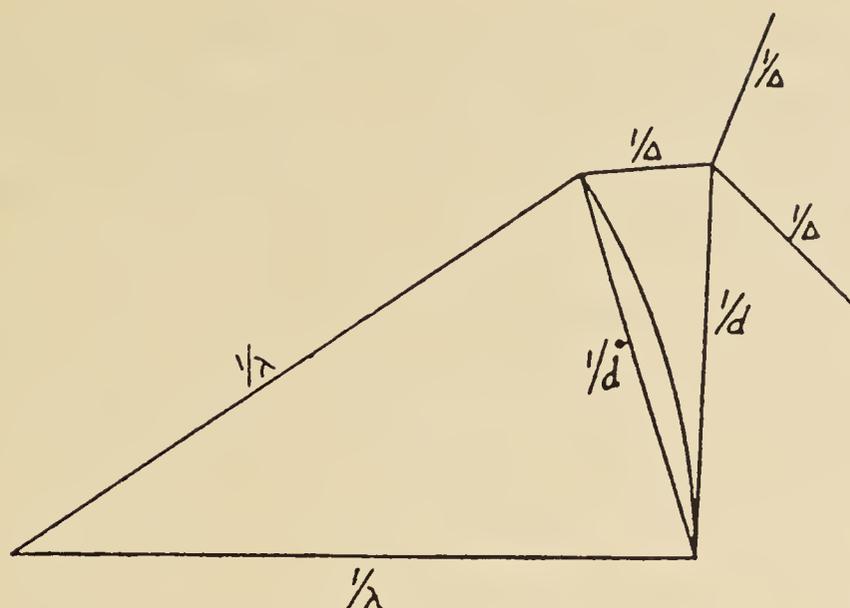


Figure 4. Geometry of quantum reflection.

case (figure 4) from that of quantum scattering also represented geometrically in figure 2. Such a restriction arises naturally from the fact that we are now concerned, *not* with a displacement of the lattice cell as a whole in some *arbitrary direction*, but with a *specific* mode of vibration of the atomic grouping within the cell. The symmetry of such atomic grouping, the nature and magnitude of the interatomic forces and especially the geometrical characters of the particular mode of vibration are superposed, or when the binding forces in the crystal are relatively the ideal case, therefore, we may expect this to lie in one or another of certain *precisely* defined directions related to the symmetry of the crystal and the symmetry of the mode of vibration. The quantum reflection would then appear, as indicated in figure 4, in a *sharply defined* direction (or in sharply defined directions, if, for instance, considerations of symmetry require that there should be several possible directions of the vector δ). It is evident that such a restriction of the phase-vector δ to specific directions would result in a very great increase in the intensity of the observable effects; in fact, the sharper the reflection, the more intense it would be and therefore the more easily observed. Thus, even if only a small fraction of the total number N of possible modes of vibration appear as stragglers from the point $\delta = 0$, their restriction to specific directions of δ should enormously increase the visibility of their effects.

We cannot however always expect the dynamic reflections to exhibit the same sharpness and precisely defined geometric character as the static reflections by the crystal planes. When, for instance, the effects of different possible modes of vibration are superposed, or when the binding forces in the crystal are relatively weak and are further disturbed by thermal agitation, a certain lack of precision in the direction of the phase-vectors would be inevitable. In such a case, the quantum reflections would necessarily be a little diffuse. Since, however, the majority of values of the vector δ congregate at the point $\delta = 0$, all the possible directions of the vector must necessarily crowd together as we approach the common origin. Hence, the reflections should appear not only more intense but

also more sharply defined as the crystal setting approaches the position in which the static and dynamic reflections coincide. The same considerations indicate that at the lowest possible temperatures when the disturbing influence of thermal agitation is removed, the diffuseness, if any, of the quantum reflections arising from its presence should diminish and disappear.

As indicated in earlier discussions, the distribution of the N possible modes of vibration amongst various values of the phase-wave vector δ is closely connected with the perfection of the monochromatism of the vibration frequency. The distribution should, in fact, run parallel to the distribution of the N modes amongst the various possible frequencies of vibration. The fine structure of the spectral lines in the infra-red region should thus stand in the closest relation to the variation in intensity of the quantum X-ray reflections with the crystal setting. It is known from studies on light scattering that the spectral lines representing the lattice vibrations, especially those of the lowest frequencies, become sharper at low temperatures. This effect is presumably due to the removal of the thermal agitation which disturbs the precisely defined geometric character of the infra-red vibrations and therefore also their monochromatism. Observations at low temperature should thus indicate a closer approach of the X-ray effects towards the ideal behaviour, viz., the appearance of sharply defined and correspondingly more intense dynamic reflections. Whether temperature directly affects the distribution of the N possible modes in the δ diagram, in other words tends to transfer a larger proportion of the modes to the origin $\delta = 0$, thereby diminishing the number of stragglers must, for the present remain, an open question. It can only be answered when we are in a position quantitatively to formulate the distribution law. The strength of the inter-atomic bindings within the lattice cell, and the strength of the forces which link the lattice cells to each other and make the whole crystal a coherent solid must necessarily enter into such a distribution law. Only in the ideal case when the lattice cells are firmly linked with each other and the influence of thermal agitation is negligible would be the assumption that the atoms within the lattice cells all vibrate together with identical frequency, amplitude, and phase approach towards the complete truth. It follows that our calculation of the intensity of the quantum reflection from equations (27) and (28) should be regarded as setting an upper limit to the intensity of such reflections which would be approached only in the most favourable cases.

8. Temperature factor for quantum reflections

The quantum theory of radiation is an application of quantum mechanics to a consideration of the interrelations between matter and radiation. In our present problem we are concerned with the effect of passage of a train of waves through a regularly stratified medium in the particular case when the stratifications, may, in part, be time-periodic. If the existence of such time-periodic stratifications be

assumed, classical optics indicates – quite independently of all atomistic or quantum theoretical considerations – that both static and dynamic reflections would be observable under appropriate conditions, the latter appearing with a change of frequency. We translate this result into the language of the quantum theory by saying that the change of frequency arises from the exchange of energy between the photon and the medium, while the optical condition for a dynamic reflection is equivalent to the conservation of momentum in their encounter (Tamm 1930). Quantum theory indicates that there is a finite probability of a vibration quantum being created or destroyed in the encounter if there be a finite interaction energy between the radiation field and the vibrations of the solid. The fundamentally new feature arising in the quantum mechanics not indicated by the classical or semi-classical theories is that the vibrations, even if non-existent in the absence of the radiation, would be created by it. This is the basis of our equation (27) in which the energy of the oscillation is put equal to $h\nu^*$ and which correctly represents the situation at the lowest temperatures. In the presence of thermal agitation, we have to merely add a contribution due to its effect. In other words, instead of $h\nu^*$ we write the energy of the vibration in equation (27) as

$$h\nu^* \left(1 + \frac{1}{\exp(h\nu^*/KT) - 1} \right). \quad (29)$$

The second term within the brackets is the Planck factor. The justification for its inclusion is that the probability of the creation of a vibration quantum would be proportional to the number of such quanta present, and (29) is therefore only valid when we are considering encounters in which the number of vibration quanta is *increased* by the incidence of radiation. In considering the cases in which the number is *diminished*, we must evidently take the energy as

$$h\nu^* \cdot \frac{1}{\exp(h\nu^*/KT) - 1} \quad (30)$$

In our present problem, the effects of both types of encounters appear superposed, and we may therefore take the energy as the sum of (29) and (30), viz.,

$$h\nu^* \cdot \frac{\exp(h\nu^*/KT) + 1}{\exp(h\nu^*/KT) - 1}. \quad (31)$$

The effect of thermal agitation would be thus to increase the intensity of the quantum reflection or the quantum scattering as the case may be, by the factor

$$\frac{\exp(h\nu^*/KT) + 1}{\exp(h\nu^*/KT) - 1}, \quad (32)$$

which we shall refer to as the temperature factor in what follows.

In the particular cases when $h\nu^* \gg KT$, viz., when the frequency of vibration is very high or the temperature is very low, the temperature factor reduces to unity

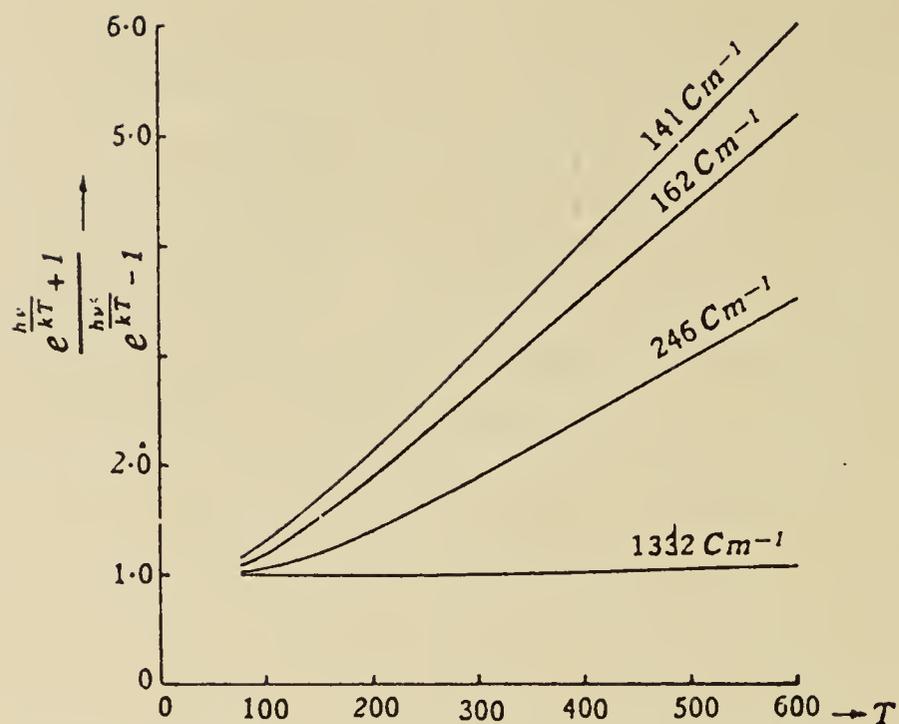


Figure 5. Temperature factor of quantum reflection.

and (31) becomes simply $h\nu^*$. On the other hand, when $h\nu^* \gg KT$, viz., when the frequency of vibration is very low or the temperature is very high; the expression (31) reduces to $2KT$. The numerical factor 2 indicates that we are now dealing with the sum of the two effects having the frequencies $(\nu \pm \nu^*)$, whereas previously we are only concerned with $(\nu - \nu^*)$. Thus, at sufficiently high temperatures, the intensities of dynamic reflection and scattering become proportional to the absolute temperature. At what stage this occurs depends on the value of ν^* . To illustrate this feature, the value of the temperature factor has been drawn as a function of the absolute temperature in figure 5 for a number of different values of ν^* . These are indicated in each case in spectroscopic units against the curves. It will be seen that all the curves tend asymptotically to the value unity at low temperatures. For low values of ν^* , the curve begins to rise steeply at a fairly low temperature, while for high values of ν^* , it remains nearly horizontal over a large range of temperature.

The foregoing is, of course, a simplified treatment, but it is sufficient to indicate the main features of the case. The treatment assumes that the intensity of dynamic reflection is proportional to the energy of the vibration giving rise to it. Such proportionality does not necessarily hold good when the thermal agitation is too violent. It should also be remarked that we are considering the different possible modes of infra-red vibrations as independent of each other, in other words, we are neglecting their mutual influence. Even when such neglect of the interactions is justified, we must necessarily consider their effects as superposed on each other. When there are several infra-red modes of widely different frequencies, it is possible that the temperature factor may be effectively different for the different sets of lattice planes in the crystal. In other words, those lattice planes whose structure amplitude is noticeably affected by the infra-red vibrations of lowest

frequency would show a large temperature factor, while those which are sensibly influenced only by the modes of higher frequency would show a relatively small temperature variation. That such a situation would arise in crystals which are highly anisotropic in structure is extremely probable. That it may occur even in isotropic crystals becomes evident when we recall that the atomic density and the structure amplitude vary enormously for the different planes of a crystal. Some of the planes in a crystal have special properties, e.g., cleavage, determined by the grouping of the atoms and the nature of the atomic bindings. These factors also determine the modes of atomic vibration possible. Hence, it should not be a matter for surprise to find that the temperature factor for dynamic reflection varies greatly for different planes also in isotropic crystals.

9. Temperature factor for classical reflections

We have already noticed in section 5 that the presence of a vibration which endows the lattice units with a dynamic structure factor simultaneously results in a reduction of the static factor. The reduction arises from the term $J_0(\zeta_p)$ which multiplies the atomic structure factor, this being the same for all the p atoms in the unit cell in the case of an elastic vibration, but different for the p different atoms in the case of an infra-red vibration. The energy of an *individual* vibration being only $h\nu^*$ multiplied by the relevant factors, see (29) and (30), the diminution of the static structure factor produced by it is negligible. The infra-red vibrations, however, have an N -fold degeneracy. The vibration of the atoms resulting from the superposition of the N modes would therefore be sensible and therefore also the diminution of the static structure factor produced by it. When the static reflection appears, the dynamic reflection is also superposed on it and is therefore effectively an addition to its intensity. Nevertheless, if the intensities of the two types of reflection are assumed to be proportional to the squares of their respective structure factors, the diminution of intensity is not compensated by such superposition. In other words, *the possibility of a quantum X-ray reflection by the crystal planes necessarily diminishes the intensity of the classical X-ray reflections by the same planes.*

In practice, there may be several modes of infra-red vibration possible. Their effect and also the *aggregate* effect of the low-frequency elastic vibrations of the lattice on the static structure factor of the atoms requires consideration. We therefore proceed to examine the case in which several different modes of vibrations are superposed. We write for the displacement of the p th atom.

$$D_p = d_p + \sum_n \alpha_{pn} \cos(2\pi\nu_n^* t + z_{pn}). \quad (33)$$

The secondary radiations from the atom have then as their periodic part

$$\cos \left[2\pi\nu t - Z_p - \sum_n \zeta_{pn} \cos(2\pi\nu_n^* t + z_{pn}) \right]. \quad (34)$$

The expansion of this in a series of Bessel functions is most easily carried out by writing (34) in an exponential form. It then appears as a product of a series of terms containing ν , ν_1^* , ν_2^* , etc., in the exponentials. On writing out the products after expansion in a series of Bessel functions, we get terms which are periodic in ν , $(\nu \pm \nu_1^*)$, $(\nu \pm \nu_2^*)$, etc., and also periodic terms involving overtones and combinations of ν_1^* , ν_2^* , etc. Neglecting these latter, the multiplier of the atomic structure factor for the frequency ν comes out as

$$\prod_n J_0(\zeta_{pn}). \quad (35)$$

While the multiplier for the atomic structure factor for the frequency $(\nu \pm \nu_m^*)$ is

$$J_1(\zeta_{pm}) \cdot \prod_{n \neq m} J_0(\zeta_{pn}). \quad (36)$$

For values of ζ which are not too large, we may use the approximation

$$J_0(\zeta) = \exp\left(-\frac{1}{4}\zeta^2\right) \quad \text{and} \quad J_1(\zeta) = 12\zeta. \quad (37)$$

Thus, the multiplier for the static structure factor of the atom is

$$\exp\left(-\sum_n \frac{1}{4}\zeta_{pn}^2\right), \quad (38)$$

the summation in the exponent being over all the n different frequencies of vibration. The multiplier for the dynamic structure factor of the atom for the frequency $(\nu \pm \nu_m^*)$ is

$$\frac{1}{2}\zeta_{pm} \cdot \exp\left(-\sum_{n \neq m} \frac{1}{4}\zeta_{pn}^2\right), \quad (39)$$

the summation in the exponent being now made over all the frequencies of vibration except ν_m^* . It appears from (38) that all the modes of vibration assist in diminishing the static structure factor, while (39) indicates that the dynamic structure factor for a particular frequency of vibration is diminished in the same way by all the other modes of vibration. The ratio of (39) to (38) is

$$\frac{1}{2}\zeta_{pm} \cdot \exp\left(-\frac{1}{4}\zeta_{pm}^2\right), \quad (40)$$

and depends only on the displacements of the atom due to the vibration of frequency ν_m^* . In this particular sense, each different vibration may be regarded as acting independently of all others, in other words as giving a quantum reflection of which the intensity in relation to the classical reflection is determined exclusively by its own amplitude.

In the summation indicated by the exponent in (38), we have to include all the frequencies of vibration of the lattice. We recall that

$$\zeta_{pn} = \frac{4\pi\alpha_{pn} \sin \theta}{\lambda}, \quad (41)$$

where α_{pn} is the displacement of the p th atom resolved normal to the crystal plane due to the vibration of frequency ν_n^* , the actual displacement ξ_{pn} being given by the geometry of the vibration and its energy. Considering the elastic vibrations first, we have already noticed that those of the lowest frequencies give the largest atomic displacements. On the other hand, the modes of the higher frequencies are far more numerous. Thus, the entire range of possible frequencies of elastic vibration would contribute towards determining the product (38) which alters the atomic structure factor. The treatment of the problem by Debye, Waller and Laue however greatly exaggerates the part which the elastic vibrations of the lattice play in this respect. Firstly, there is no justification for assigning all the $3Np$ degrees of freedom to the elastic vibrations. The maximum number which can properly be so assigned is $3N$, the remaining $(3p - 3)N$ degrees of freedom representing the infra-red or monochromatic vibrations of the lattice. Then again, the actual frequency limit for the elastic spectrum is automatically reduced by the diminution in the number of degrees of freedom allotted to it. Thirdly, the semi-classical way in which the quantum theory of specific heats and the zero point energy are usually brought into the X-ray problem is, of course, invalid. Finally, in the vast majority of actual crystals, the Einstein or monochromatic vibrations, besides being more numerous, have often quite low frequencies and therefore make a notable contribution to the thermal energy. Their influence on the intensity of the classical reflections indicated by (38) should therefore be of great importance, in fact much more so than that of the elastic vibrations of the lattice.

It follows from what has been stated above that there should be a considerable degree of correlation between the intensity of the quantum reflection by a particular set of crystal planes and the temperature variation of the intensity of the classical reflection by the same set of planes. An intense quantum reflection can only arise if the structure amplitudes are strongly influenced by the possible modes of infra-red vibration with a corresponding diminution of the static structure factor. We should then ordinarily expect a notable temperature effect of the intensity of classical reflection, *pari passu* with an increase of the intensity of quantum reflection with rising temperature. Since however, the static and dynamic structure factors for the unit cell are determined by different considerations, the factors for the unit cell are determined by different considerations, the correlation indicated above is not necessarily to be observed in all cases.

10. Summary

The ideas indicated in the preceding paper are here worked out quantitatively. The secondary radiation from an oscillating atom in a crystal traversed by X-rays is analysed into its frequency components. It is shown that the interferences to which each component of altered frequency gives rise are determined jointly by

the positions of the atoms and the phases of their vibration. It follows that besides the static reflections of unmodified frequency by the crystal planes, we would also have dynamic reflections of altered frequency. The geometric law of such dynamic reflection is derived. The static and dynamic structure factors are deduced and it is pointed out that the elastic and infra-red vibrations of the lattice stand on a different footing in respect of these factors. Considering first the elastic vibrations, formulae are obtained and graphs are drawn which show that such vibrations give rise to a diffuse scattering of the X-rays with low intensity proportional to the number of lattice cells. The N-fold degeneracy of the monochromatic infra-red vibrations, on the other hand, results in their giving true geometric reflections with altered frequency and with intensity proportional to the square of the number of lattice cells. The intensity of such reflection is evaluated on the basis of the quantum theory of radiation. The variation of the intensity, direction and sharpness of the quantum reflections with crystal setting is discussed. A formula is then obtained for the temperature variation of the intensity of the quantum reflections. The temperature factor for the intensity of the classical reflection is also written down and the extents to which the elastic and infra-red vibrations respectively contribute to it are discussed.

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Quantum theory of X-ray reflection: experimental confirmation

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1. Introduction

The fundamental discovery that the lattice planes in a crystal give rise to monochromatic X-ray reflections of a second kind involving a change of frequency was made in the laboratories of this Institute and announced at the Easter meeting of the scientific societies of Bangalore held on the 22nd March 1940. It was an essential part of the discovery that the experimental characters of the phenomenon as actually observed were such as to place it entirely outside the range of the accepted theories in X-ray optics. The explanation of the newly discovered phenomena, in fact, demanded the introduction of radically new ideas regarding the nature of the vibrations possible in crystal lattices and also regarding the nature of the interactions which occur when X-rays traverse a crystal. These new ideas were indicated simultaneously with the new experimental facts in an article in *Current Science* for April 1940. Though new to X-ray physics, the ideas set out in that article had already emerged more or less clearly

from the spectroscopic investigations on the scattering of light in crystals which had previously been engaging the attention of the laboratory.* The application of these ideas in the field of X-ray research was thus almost inevitable. The further investigations which have since been continued systematically at this Institute have not merely confirmed the statements made in the first publication, but have also shown that the new X-ray results taken together with the earlier spectroscopic studies compel revolutionary changes in our concepts of the solid state. In fact, the X-rays directly demonstrate what had been previously only inferred from the optical evidence, namely, that the lattice vibrations appearing as monochromatic lines in the spectrum of a crystal possess a degree of orderliness and coherence which is astonishing and truly as remarkable as the orderliness of the static arrangement of the atoms characteristic of a crystal. The optical and X-ray methods of investigating the lattice vibrations in crystals thus stand in the closest relation, supplementing each other. The optical methods enable us to analyse the infra-red vibrations into their frequency spectrum and only indirectly to infer their geometric character. The X-rays, on the other hand, enable us directly to ascertain the geometrical characters of the vibration and only indirectly to infer the frequency changes involved.

The clear-cut enunciation of the new facts and ideas put forward in April 1940 was made possible largely by the deliberate choice of diamond as the crystal round which the investigations have principally centred. The known perfection of this crystal, the simplicity of its structure, the possibility of using relatively soft X-rays in working with it, and above all, the geometric precision with which it exhibits the new phenomena have enabled the latter to be understood much more clearly than would have been otherwise possible. For this reason, the present article will be devoted wholly to the results of the experimental studies made with diamond. It will be shown, on the one hand, how the experimental facts totally exclude any explanation of the type based on the original theories of Debye, Waller and Faxén, with or without such further modifications as have been recently suggested. It will, on the other hand, be shown how completely the experimental facts fit into the scheme of new ideas expounded and developed quantitatively in the two preceding papers. It must not be imagined however that the case for the new theory rests exclusively on the facts observed with diamond. So far from this being the case, it may be said that a careful and unprejudiced examination of the facts with any crystal is sufficient to show that the efforts recently made by several workers, notably Zachariasen, Max Born and the group at the Royal Institution to base an explanation of the new X-ray facts observed at this Institute on the basis of the existing theories or modifications thereof are not on the right lines. In the earlier paper on basic ideas, the effects indicated by the

*A brief summary of these investigations and the ideas emerging therefrom will be found in the Franklin Medal Day lecture to be published in the *Franklin Institute Journal* for September 1941.

theories of the Debye type are set out and contrasted with those indicated by the quantum theory of X-ray reflection, and a series of experimental criteria are put forward enabling a discrimination between the two. In the papers which follow in these *Proceedings*, these criteria have been applied in several cases, and in every case the verdict of the facts has been in favour of the new ideas. Equally striking has been the success of the new ideas in dealing with problems of the solid state which have hitherto proved baffling, e.g., the large deviations of the observed specific heats of elementary solids, such as metals, from those indicated by the Debye specific heat formula. Far from such a failure of the Debye theory being surprising, it is a necessary consequence of the idea that the lattice spectrum of every crystal includes Einstein or monochromatic frequencies of vibration. Mr Bisheswar Dayal has shown in a series of papers which will appear in the next issue of these *Proceedings* that the specific heat curves for metals and other elementary solids find a very simple and complete examination on the basis of these new concepts in crystal dynamics.

2. Structure and lattice spectrum of diamond

The specific heat of diamond has been accurately measured by Pitzer (1938) over the range of temperature from 70° T to 288° T . His data do not fit into the Debye formula, showing deviations as large as fifteen percent within this range, if the limiting frequency in the formula is chosen to fit the data at the lower limit of temperature. The cause of this failure becomes apparent when we consider the real nature of the lattice spectrum. The Debye theory of specific heats rests on the belief that the infra-red vibrations of the lattice are physically of the same nature as the vibrations of the acoustic type and form a continuous spectrum of frequencies. That the same idea forms the basis of the crystal dynamics of Max Born and his school is evident from the postulate of the "cyclic lattice" on which the work of that school rests and which has been discussed earlier in these *Proceedings* and shown to be untenable. The Born postulate places the elastic and infra-red vibrations mathematically on the same footing. Its implications become clear when we examine the results of the calculations worked out on its basis by Blackmann, Kellerman and others of that school. The calculations lead to representations of the vibration spectrum which while differing in detail from that assumed in the Debye theory, have nevertheless the same fundamental feature, namely that the vibrations of the extended solid forms a continuous spectrum of frequencies. The lattice spectra of actual crystals as revealed to us by spectroscopic investigations, especially those made at low temperatures, present us with a totally different picture. Indeed, it may be said that the assumptions made in the Debye theory and in the Born crystal dynamics bear no resemblance whatever to the actual facts at such temperatures.

Several different lines of investigation agree in showing that, except possibly in

the region of the lowest frequencies where the experimental techniques have not at present been good enough to give a definite answer, the lattice spectrum of diamond consists of sharply defined or monochromatic frequencies. Bhagavantam (1930) investigated the scattering of light in diamond and found numerous sharp lines in the spectrum giving the following frequency shifts in wave numbers per centimetre: 1585, 1480, 1431, 1382, **1332**, 1288 and **1158**. Amongst these, the 1332 line is at least a hundred times more intense than the next most intense line 1158, while the others were just detectable in the spectrum of a large clear white diamond. The 1332 line, besides being intense, is also extraordinarily sharp, in fact exactly as sharp as the exciting radiations. It remains sharp (though with gradually diminishing frequency shift) over the whole range of temperature from 93°T to 1130°T . Further evidence on the lattice spectrum of diamond has been furnished by the recent investigations of Nayar at this Institute on its luminescence and ultra-violet absorption spectra at low temperatures. As was first noticed by Ramaswamy, diamond exhibits a fluorescent band at 4157 A.U., the same band also appearing in absorption. On cooling down the crystal to liquid-air temperatures, this band shifts to 4152 A.U., at the same time becoming much sharper. Subsidiary bands are also noticed at lower frequencies in fluorescence and at higher frequencies in absorption, the frequency differences between these and the 4152 band being the same but of opposite sign in fluorescence and in absorption. These frequency differences therefore represent the lattice spectrum of diamond. The band at 4152 A.U. is not as sharp at liquid-air temperature as could be desired, and it is greatly to be hoped that this work will be repeated at liquid hydrogen temperatures in some cryogenic laboratory. Nevertheless even at liquid-air temperatures and using the fairly high dispersion provided by an E_1 Hilger spectrograph, Nayar has found that the fluorescence and absorption bands appear resolved into numerous *discrete frequencies*. These are (within about ten wave numbers) 1341, 1252, 1148, 1090, 1010, 960, 784, 681 and 532. These are indications of larger frequency shifts in the same region as those observed by Bhagavantam, as also of several discrete frequency shifts smaller than 532 appearing very feebly in the spectra. Plate I, figures 4(a), (b) and (c) reproduce the lattice spectrum of diamond as observed respectively in light-scattering, in fluorescence and in absorption, and exhibit these frequency shifts.

The dynamical theory of the diamond lattice has not at present been worked out with sufficient thoroughness to enable us to explain all these experimental results. It is noticed, however, that the most intense fluorescence and absorption frequencies fall roughly into two groups. The head of one of these groups is close to the 1332 frequency which appears as an extremely intense and sharp line in light scattering. The nature of the 1332 vibration has been very fully discussed by Nagendra Nath (1934) and was indicated by him as an oscillation relative to each other of the two Bravais lattices of carbon atoms which constitute diamond. Since each carbon atom belonging to one lattice is bound by valence bonds to four

carbon atoms in the other lattice, and vice versa, such an oscillation would necessarily have a high frequency. Indeed, a calculation based on the known force constants gives a frequency in fair agreement with the observed 1332. The symmetry characters of such an oscillation (Venkatarayudu 1938) also indicate that it should be active in light-scattering. The identification of the 1332 frequency as that of an oscillation of the two interpenetrating lattices of carbon atoms relative to each other is thus firmly established. The second group of frequencies of which the head is at 784 is completely inactive in light scattering. It is therefore very probable that the oscillations of this group involve movements of the atoms in each Bravais lattice against themselves, alterations of the tetrahedral valence angles rather than the extensions or compressions of the valence bonds determining the observed frequencies.

Examining the structure of diamond, we find that the carbon atoms belonging to the two Bravais lattices appear in the planes parallel to the octahedral faces in separate layers which are alternately at *unequal distances*. It follows from this fact and the considerations set out in the preceding paper that the (111) planes would have their structure amplitudes strongly varied by the 1332 oscillation. A similar situation would also arise in respect of any oscillation in which the movements of some of the atoms in one Bravais lattice are balanced by opposite movements of an equal number of atoms in the other lattice. If, on the other hand, we consider a type of vibration in which the movements of the atoms in one lattice are balanced by opposite movements of the remainder of the atoms in the same lattice, it is easily seen that the structure amplitudes of the octahedral planes would remain unaffected. It is thus evident that only the 1332 vibrations or other vibrations of similar character would influence the structure amplitudes of these planes. A simple calculation on the basis of the theory set out in the preceding paper shows that in spite of the high frequency involved in such oscillations, dynamic reflections of notable intensity should be given by the (111) planes. On account of the high frequency of the associated vibrations of the lattice, such reflections should be practically insensitive to variations of temperature.

The crystal spacings in diamond giving the classical X-ray reflections are of two kinds. In one set which includes the spacings parallel to the octahedral faces, the alternate layers of carbon atoms appear unequally spaced in the ratio of 1:3. In the second set, which includes the planes parallel to the forms of the cube and the dodecahedron, the planes appear equally spaced. In the planes parallel to the dodecahedral faces, the carbon atoms belonging to the two Bravais lattices appear interspersed with each other in equal numbers. It follows that these planes are incapable of giving a dynamic reflection as a result of the relative oscillation of these two lattices. This conclusion, however, only refers to this particular mode of vibration having the high frequency of 1332 wave-numbers. There are numerous other modes of vibration of the lattice with discrete frequencies, some of which are as low as 127, 178, 303 and 421 wave-numbers (Nayar 1941). In such vibrations, there can be no doubt that the atoms in each Bravais lattice oscillate against each

other, that is, some of the atoms move one way and the others move the opposite way to balance the oscillation. The extreme feebleness with which the frequencies lower than 532 appear in fluorescence and absorption probably indicates that such vibrations have a relatively small a priori probability. Nevertheless, a low frequency involves a correspondingly larger amplitude of vibration. Hence, the planes in the crystal which cannot give a dynamic reflection associated with the 1332 vibration may nevertheless give observable reflections associated with some of the vibrations of the lattice with lower frequencies. Such reflections would be indicated by their intensity being more temperature-sensitive than the reflections associated with the high-frequency vibrations.

3. Specular character of quantum reflections

Amongst the many items of supporting experimental evidence set out in the publications by the present writers (1940) announcing the discovery of quantum or modified reflection, one of the most cogent which was duly emphasized was the truly geometric or specular character of the reflections associated with the (111) planes of diamond. This feature by itself and apart from all other evidence was sufficient proof that the phenomena described in those papers lay entirely outside the scope of X-ray optics as it existed before the announcement of the discovery. In view of the importance of this feature and especially of the fact that it is absolutely fatal to the attempts made by Max Born and others to interpret the phenomena on the basis of the Debye–Born crystal dynamics, we shall here consider it in some detail.

Even in the photographs published with our earliest communications (*Current Science*, April 1940 and *Nature*, 27th April 1940), it was evident that the quantum or dynamic reflections given by the (111) planes of diamond were just as sharp as the ordinary Laue reflections by the same planes. While the Laue reflections appeared as elliptic spots, the quantum reflections were round in shape and had about the same diameter as the major axis of the Laue spots. These features are readily understood when the angular divergence of the incident beam is considered and it is borne in mind that a quantum reflection can occur at any incidence of the X-rays on the crystal planes. A detailed discussion of the geometric aspects of the quantum X-ray reflections in diamond by Mr P R Pisharoty has already appeared in a recent issue of these *Proceedings* (1941). Mr Pisharoty has proved that the appearance of the quantum reflections as observed in the photographs for all possible settings of the crystal is just what we should expect if they were perfectly geometric.

In actual experimental work with X-rays, the radiation from the source is necessarily divergent. The extent and manner in which such divergence may be advantageously limited depends both on the aim of the investigation as well as

upon the material under study, viz., upon the thickness or area of the crystal. In investigating phenomena of low intensity, an undue restriction of the divergence of the beam would merely increase the difficulties of the investigation without advancing its purposes in any way. Thus, for instance, in the present problem, when we wish to decide whether we are dealing with a sharp reflection or a diffuse scattering, instead of reducing the aperture excessively, it is preferable to retain it at a reasonable value and prolong the photographic exposures as much as possible. In such circumstances, a geometric reflection would not enlarge in area, while a diffuse scattering would progressively widen out. Using the technique here indicated, it is easy to decide the question whether the quantum reflections in diamond enlarge their angular extension when the crystal is moved away from the setting at which the quantum and classical reflections coincide. By not reducing the width of the X-ray beam unduly, it is possible to record the spots with fair intensity even when the crystal setting is altered by as much as 6° in either direction. It will be seen from the photographs reproduced in plate II, figures 5(a) to (k) that the extension of the quantum reflections remains constant over this whole range of settings, while if it were due to a scattering of the X-rays associated with the reflections of the usual kind, it should enlarge rapidly in area. One has only to glance at the photographs in figure 5 and then turn to the set of curves reproduced in figure 3 of the preceding paper showing how the distribution of intensity of scattering of X-rays varies with the setting of the crystal to realise the futility of any attempt to explain the actual phenomena in terms of the scattering theory.

The classical and quantum reflections have a different origin and obey different geometric laws. Nevertheless, they are both geometric reflections, and optical principles indicate various simple criteria which can be employed to test their nature as such and which would reveal the correct position immediately if the quantum reflection were not an independent phenomenon. Various factors in the experimental technique are capable of variation, e.g., the area and angular divergence of the incident X-ray beam, as well as the area and the thickness of the crystal irradiated by it. These variations would influence the intensity and the angular spread of the two effects in a very different manner if they were not essentially similar phenomena. Actually, we observe a complete parallelism in the behaviour of the classical and quantum reflections when the experimental factors are varied separately or together. It is well known, for instance, that the spots in a Laue pattern diminish in extension when the X-ray beam is made narrower, and that such diminution in size cannot be prevented from occurring by merely prolonging the photographic exposures. Precisely the same effect is observed with the quantum reflections by the (111) planes in diamond. These are reduced in extension by limiting the area of the X-ray pencil in much the same way and in the same proportion as the ordinary Laue reflections, longer exposures not altering the situation. It is also noticed that the relative intensity of the Laue and quantum reflections remains unaltered by such procedure, thus proving that we are dealing

with true geometric reflections in both cases and not a reflection in one case and a scattering in the other.

The classical X-ray reflections by the lattice planes of crystals appear in directions which are geometrically definable with a degree of precision depending on the perfection of the crystal. Diamond, for instance, may be so perfect that the setting at which it reflects monochromatic rays with the maximum intensity is probably definable with as great an accuracy as the wavelength can itself be specified. In the case of the quantum reflection, we are concerned not only with the geometric perfection of the crystal but also with its *spectroscopic* perfection, that is to say, with the monochromatism of the infra-red vibrations of its lattice. As will be seen from figure 4(a) in plate I, the monochromatism of the 1332 vibration of the diamond lattice, even at ordinary temperature, is of the most remarkable kind. Accordingly, we should expect that the quantum reflections by the (111) planes which owe their origin to it should have a precisely definable geometric character and should be unaffected in their sharpness by the setting of the crystal. A rigorous test of this question is not so easy as in the case of the classical reflections, for the quantum reflections can occur independently of the angle of incidence of the X-rays on the crystal. Hence, an angular divergence of the incident beam and therefore also of the reflections can easily be mistaken as indicating a lack of geometric perfection of the latter. The severity of the test which can be made depends on the possibility of obtaining an X-ray beam with small lateral extension and angular divergence but of sufficient intensity to record the quantum reflections in a reasonable time. As the intensity of the reflections falls off with extreme rapidity when the crystal setting is turned away so as to separate the classical and quantum reflections, it is evidently not easy to push the question to the final limit. It may be stated, however, that *the quantum reflections by the (111) planes of diamond are geometrically as perfect as can be experimentally ascertained at the present time*. This is shown by the photographs reproduced by figures 6(a) and (b) in plate III. In these photographs, the quantum reflections by the (111) planes have been recorded using a fine rectangular slit 100 millimetres deep and 0.15 millimetre wide, and a cleavage plate of diamond 0.76 millimetre thick. The width of the reflections as measured on the plates is no greater than that to be expected from the finite lateral extension of the beam, its angular divergence and the thickness of the plate used. It is specially noteworthy that the reflection as recorded on the plates shows no detectable widening when the crystal setting is altered so as to make the quantum reflection move away from the Laue reflection in one direction or the other by several degrees.

These facts show that there is no ground for the belief entertained by some X-ray workers in the Debye–Waller–Faxén theory of X-ray scattering as a possible explanation for the phenomena discovered with diamond at this Institute. So striking are the facts that even the advocates of the scattering theory have been compelled to take the illogical step of referring to the phenomena as a “diffuse reflection” instead of as a “diffuse scattering” which would be the correct

nomenclature for them to adopt on the basis of that theory. Indeed, the designation of “diffuse reflection” as applied to the case of the (111) quantum reflection of a diamond is quite misleading. Actually, these reflections are probably as sharp or sharper than the classical reflections of X-rays by the lattice planes of many crystals of the ordinary or imperfect type.

4. Geometric law of quantum reflection

Any discussion regarding the geometric law of the quantum reflection presupposes its specular character. Indeed, unless we are dealing with a phenomenon which is recognizable as a reflection over a wide range of settings of the crystal and whose position can be observed and stated with some precision, there can be no point in discussing the validity of any geometric formula descriptive of it. No useful purpose would be served, for instance, in seeking to find empirically the point of maximum intensity in a field of diffuse scattering such as those represented theoretically in the curves of figure 3 of the preceding paper. The precision with which the position of the X-ray reflections can actually be located and measured is an indication that the experimental situation in this respect is very different indeed from that arising in the case of X-ray scattering.

The earliest measurements made with diamond (Raman and Nilakantan, May 1940) showed that the spacing d^* of the dynamic stratifications altered rapidly with the setting of the crystal, being identical with the static spacing d of the (111) planes only at the particular setting when the two types of reflections appear superposed. It was found later that even these early measurements fitted perfectly into the general geometric law of quantum reflection

$$2d \sin \psi \sin (\vartheta \pm \varepsilon) = \lambda \sin \vartheta, \quad (1)$$

the angle ϑ coming out the same within a degree or two as the value of $54^\circ 44'$ established by the measurements over a wider range of settings of the crystal made in July and August 1940. The angle $54^\circ 44'$ is half the tetrahedral angle between the valence bonds joining the carbon atoms in diamond. It is also the angle between the faces of the cube and the octahedron in the regular crystal system. In other words, *the phase-waves for the quantum reflection of X-rays by the octahedral planes of diamond are parallel to the cube faces of the crystal*. This remarkable result which was discovered experimentally in September 1940 forms a striking confirmation of the basic ideas underlying the quantum theory of X-ray reflection. It emerged from the extended studies made in the preceding months as mentioned above. The photographs from which the measurements were made are reproduced in plate II, figures 5(a) to (k). A brief reference to this result was made in a footnote to the paper by Raman and Nath (November 1940) in which the theoretical formula (1) was first announced. The result itself was communicated in a letter to *Nature* dated the 11th November 1940 and published in its

issue of the 25th January 1941. In view of the great significance and importance of the result, it appears worth while to give a detailed account of the experimental work which led to its recognition.

These early experiments were carried out with a 'Spektro Analyst' Rontgen apparatus manufactured by Siefert & Co., Hamburg. The X-ray tube was of the sealed hot-cathode type with a copper target, the X-rays emerging through four windows of Lindemann glass. The tubes worked at 41,000 kV, with a tube current of 12 ma. A flat film type of camera was employed for taking the photographs. The X-ray beam was restricted by a circular hole bored through cylindrical lead blocks of effective depth 93 mm, the diameter of the hole being 1.6 mm.

Diamond has a perfect cleavage parallel to an octahedral face of the cubic crystal. Plates evidently obtained by cleavage in this manner and subsequently polished can be readily obtained from jewellers in India. The plate actually used was about half a square centimetre in area with a thickness of 0.76 millimetre. The crystal was mounted on the goniometer with its faces nearly vertical and nearly normal to the X-ray beam. The crystal was set by trial so that the (111) planes within the crystal from which the reflections were to be studied were vertical, as also the adjoining lattice spacings parallel to the form of the cube. Thus, when the crystal was rotated about the vertical axis of the goniometer, the plane of incidence of the X-rays on the (111) spacings remained horizontal throughout, coinciding with a plane of symmetry of the crystal parallel to the form of the dodecahedron. Particular care was taken in mounting the crystal to ensure that the goniometer axis passed through the portion of the crystal irradiated by the X-ray beam. Small rotations of the crystal introduced no sensible change in the distance from the crystal to the photographic film. This however, was checked up at every setting of the crystal. The actual distance from the diamond to the film was 3.99 centimetres for figures 5(a) to (g) and 3.95 cm for figures 5(h) to (k) in plate II. With the aperture used, the X-ray beam traversing the diamond had an appreciable angular divergence. The round shape and sharpness of the spot as recorded on the film, however, enabled the position of its centre to be located with such accuracy that the use of a finer X-ray pencil would merely have prolonged the exposures necessary and thereby increased the difficulties of the investigation without any material gain in precision.

Since, in these experiments, the reflections occur in a plane of symmetry of the crystal, it follows that we may write the geometric law (1) in the form

$$2d \sin \frac{1}{2}(\theta + \phi) \sin \left(\vartheta \pm \frac{\theta - \phi}{2} \right) = \lambda \sin \vartheta, \quad (2)$$

θ and ϕ being the glancing angles of incidence and dynamic reflection measured as usual from the crystal planes. Since the actual value of the crystal spacing is known, viz., 2.056 A.U., the most convenient representation of the data is to regard the spacing as an unknown function of θ to be determined from the

observed values of θ and ϕ and the formulae used. The angle ϑ disappears from equation (2) when $\theta = \phi$. Thus, whatever be the chosen value of ϑ , the graphs representing the calculated values of the spacing as a function of θ calculated with different assumed values of ϑ all necessarily cross at the same point. This should agree with the known spacing of the crystal within the limits of experimental error. When however, $\theta \neq \phi$, the spacing calculated would diverge progressively from the actual value unless the correct value of ϑ has been chosen. The appearance of the graph as a horizontal line in a position agreeing with the known crystal spacing thus furnishes an exact test of the formula employed.

Figure 1 shows three graphs in which the experimental observations have been set out in the manner indicated. The graph marked d_1 represents the crystal spacings calculated from the approximate formula

$$2d \sin \frac{1}{2}(\theta + \phi) = \lambda. \tag{3}$$

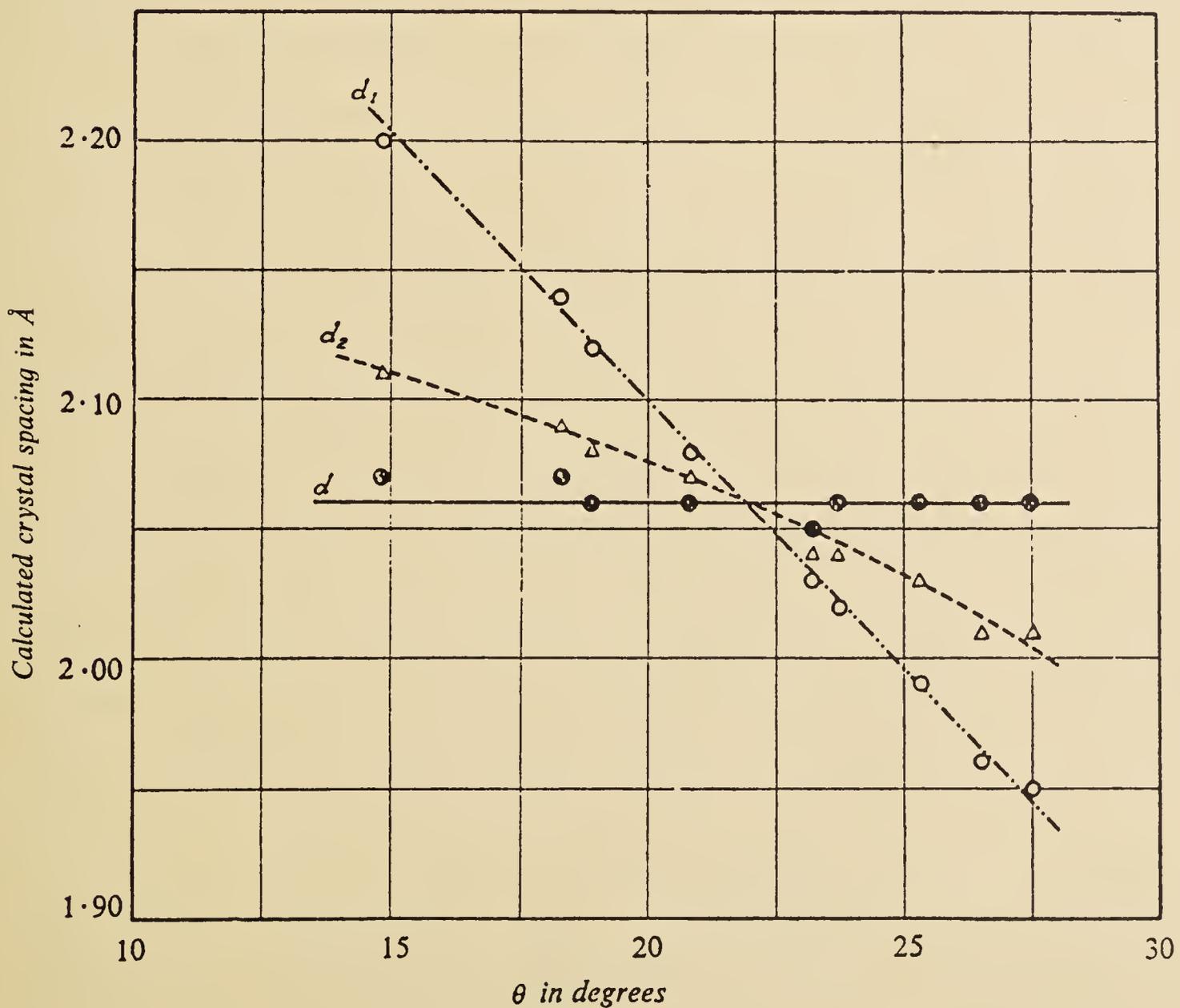


Figure 1. Geometric law of quantum reflection.

The graph marked d_2 represents the crystal spacings calculated from the formula

$$d(\sin \theta + \cos \theta \tan \phi) = \lambda. \quad (4)$$

This formula which is of the same form as that derived originally by Faxén on the basis of the scattering theory, would also represent the geometric formula of quantum reflection if the phase-waves of the infra-red lattice vibration had an arbitrary orientation within the crystal, and the actual geometric position of the reflection were determinable from a consideration of the minimum phase wavelength. The graph marked d in the figure was calculated from the formula (2) above, assuming ϑ to be $54^\circ 44'$. It will be seen that it is a horizontal straight line with a spacing very closely agreeing with the known value. On the other hand, the graphs d_1 and d_2 diverge rapidly from the known spacing at except the point where all the three graphs intersect.

To indicate the degree of accuracy with which the angle ϑ is determinable from the observations, the graphs drawn for three different values of the angle are shown in figure 2. It will be seen that the angle lies certainly within one degree of half the tetrahedral valence angle.

The experimental facts emerging from figures 6(a) and (b) in plate III, and from figures 1 and 2 above in the text are thus of a completely decisive character.

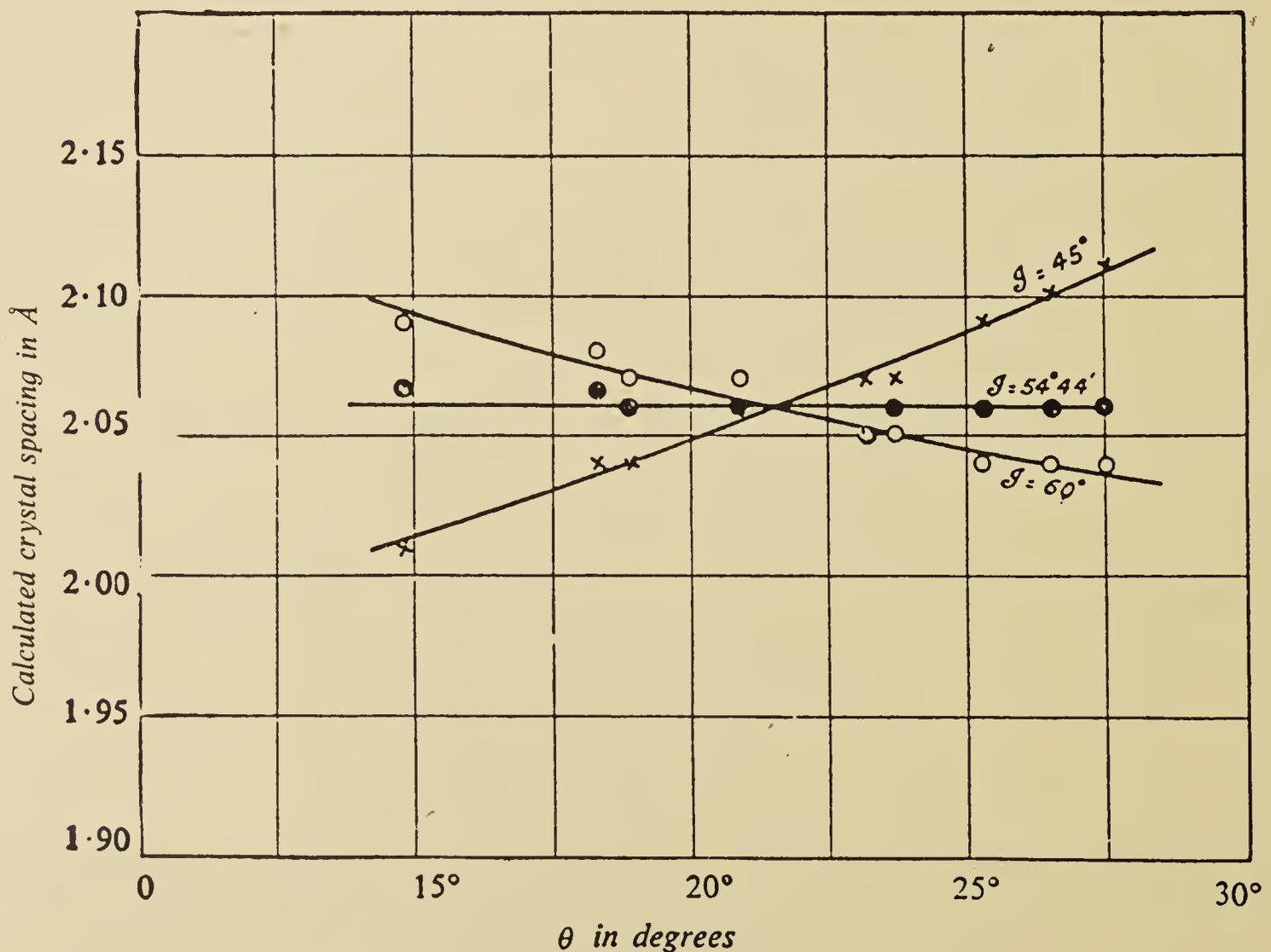


Figure 2. The inclination of the phase waves.

The Debye–Faxén–Waller theory of X-ray scattering demands a distribution of the intensity of the scattered X-rays over an area whose angular extension is expressed in as many degrees of arc as the setting of the crystal is moved away from the position required for the classical X-ray reflection. It also demands that the position of maximum intensity in such scattering, though not capable of being measured with any particular precision, should follow the course of the curve marked d_2 in figure 1. On the other hand, the actual spread of the quantum reflection is not experimentally detectable and if it is finite, is measurable in minutes of arc rather than in degrees, as indicated by figures 6(a) and (b). The geometric direction of the reflection is capable of being determined with precision and follows a wholly different law, namely that defined by equation (2) above. The facts thus definitely negative any possibility of explaining the phenomena in terms of the Debye–Faxén–Waller theory. *The observed specificity of the value of ϑ also forms a direct experimental contradiction of the Born postulate of the cyclic lattice*, since the latter assumes the phase-waves of the vibration of the crystal lattice to have all possible orientations instead of a definitely restricted orientation as shown by the X-ray results. We have thus no choice left except that of assuming the infra-red or high-frequency vibrations of the lattice to be the factor responsible for the observed X-ray reflections.

We may now consider the question why the phase-waves of the 1332 vibration which are evidently responsible for the (111) reflections are parallel to the form of the cube. The answer to this is evidently that the nature of this vibration is determined by the geometry of the crystal structure. Each carbon atom in one Bravais lattice is joined by four valence bonds in a symmetrical fashion to four other carbon atoms belonging to the other Bravais lattice. The individual valence bonds are normal to the octahedral planes in diamond, while the planes parallel to the cube faces bisect the angles between the valence bonds taken in pairs. The vibration responsible for giving the reflection by a particular set of octahedral planes is normal to them and therefore parallel to one of the valence bonds. Since the three other bonds are also possible directions for such a vibration, it is to be expected that the plane of the phase-waves would take an intermediate direction, which by symmetry should bisect the angle between them. On the basis of this argument, it is evident that there should be three sets of possible phase-waves which are respectively parallel to the three pairs of faces parallel to the forms of the cube. This result demanded by considerations of symmetry is found as we shall see presently, to be fully supported by the experimental facts.

5. The azimuth effect

A further remarkable confirmation is forthcoming for the result that the phase-waves associated with the 1332 vibration are restricted to a specific crystallographic orientation. This is the so-called azimuth effect, which was foreseen

theoretically before it was sought for and confirmed experimentally by the authors. Since the phase-waves for a (111) reflection are parallel to the adjoining cube face, it follows that if the crystal plate be rotated in its own plane so as to make the plane of incidence no longer a plane of symmetry of the crystal, the quantum reflection should move out of such plane of incidence. Why this effect occurs becomes evident when we recall that the plane in which the quantum reflection should appear is the plane of incidence of the X-rays on the dynamic stratifications; in the circumstances considered, these are no longer perpendicular to the plane of incidence of the X-rays on the static crystal planes. This situation is readily appreciated with the aid of a vector diagram in which the reciprocals of the crystal spacing and of the phase-wave normal are geometrically represented. The point at which the phase-wave normal intersects the sphere of reflection necessarily moves out of the plane of incidence when the crystal is rotated in its own plane, the angle of incidence being retained constant. It is evident that such displacement would be zero if the reciprocal phase wavelength is zero; it changes sign when the direction of the wave-normal is reversed either by a change of the crystal setting or by a change of the X-ray wavelength. In other words, the displacement of the quantum reflection out of the plane of incidence would be zero when it coincides with the Laue reflection, and would be of opposite signs when it lies respectively on the two sides of it. It should also increase progressively as the quantum reflection moves away from the Laue spot in either direction. The theory of the effect has been very fully discussed and illustrated by appropriate diagrams in the paper by Pisharoty already cited. We need not therefore enter into the matter here in further detail. The necessary mathematical formulae will be found in Pisharoty's paper. The effect is illustrated in figures 10(a) and (b) in plate IV. The angular displacements of the reflections out of the plane of incidence as measured from the photographs are in quantitative agreement with those deduced from the formulae.

6. Explanation of multiple spots and streamers

Another striking confirmation of the theory of phase-waves is afforded by the phenomena arising from the fact that there are three sets of phase-waves and therefore three quantum reflections corresponding to the points where the phase-wave normals meet the sphere of reflection. As these normals are at right angles to each other, it is not to be expected that all the three reflections would be observable in every case. The setting of the crystal would obviously determine the effects actually recorded. It is evident that if the phase-wave vector nearly grazes the sphere of reflection, the finite divergence of the incident X-ray beam would result in the reflection appearing as an oblique streak or an elongated elliptic spot, instead of as a round circular spot; the latter would be the observed result only when the vector cuts the sphere of reflection normally. The intensity of the

streamers or elliptic spots would vary with the reciprocal phase wavelength at each point, being greatest when this is a minimum and tending to zero when it is large. Hence, these streamers and subsidiary spots would be most prominent when the setting of the crystal is such that the Laue and quantum reflections nearly coincide. On the other hand, when the quantum reflection is far removed from the Laue reflections, all trace of them should disappear. These effects are well illustrated as the series of photographs reproduced in figures 5(a) to (k). A detailed discussion of them and of various other cases is given in the paper by Mr Pisharoty already cited to which the reader may be referred for further particulars. Remarkable changes in the appearances of the streamers and subsidiary spots occur when the azimuth of the setting of the crystal is altered. Some of these features are illustrated in figures 10(a) and (b) and 11(a) and (b) in plate IV, and are in full accord with the indications of the theory.

7. Intensity of quantum reflection

Extremely rapid changes occur in the intensity of the quantum reflection as it approaches from the Laue spot with an alteration of the setting of the crystal. This effect is seen in the series of pictures reproduced in figures 5(a) to (k) and is even more pronounced than would appear from the photographs since the exposures were considerably prolonged for the first few and the last few pictures of the series. A better idea of the situation is obtained from figure 7 which is reproduced from the article in *Current Science* for April 1940. It will be noticed that both the K_α and K_β reflections fall beyond the spot marked A and are so feeble as only just to be visible in the reproduction. The quantum reflection of K_α is beyond the spot marked C, while the K_β reflection actually coincides with the latter and therefore also with the classical monochromatic reflection. The spot marked C therefore appears very intense. The K_α and K_β quantum reflections appear respectively on the two sides of the spot marked B, the former being of great intensity. The illustration shows clearly that as the quantum reflection approaches the Laue spot, its intensity rapidly increases and ultimately becomes quite large.

It is evident from the pair of pictures appearing in figures 8(a) and (b) that the intensity of the quantum reflection of the monochromatic X-rays may actually exceed the intensity of the Laue reflection by the same spacings of the white radiations accompanying the characteristic X-rays of copper. That the classical and quantum reflections of the same wavelength are of comparable intensity when they are superposed is indicated by the photographs reproduced as figures 11(a) and (b) in plate IV. It will be noticed when the crystal is set so that the classical and quantum reflections coincide, the streamers emerging from the reflections on both sides are easily visible. Since these streamers are necessarily much weaker than the principal quantum reflection, it follows that the latter should be comparable in its intensity with the classical reflection of the same

wavelength which appears superposed on it. The experimental facts are thus in general accord with the conclusions arrived at from the quantum theoretical calculations set out in the preceding paper.

Experiments have also been made varying the thickness of the plate of diamond as also the width of the beam of X-rays used. These factors are found within wide limits to be without influence on the relative intensities of the classical and quantum reflections under otherwise similar conditions, thus supporting the indications of theory. On the other hand, the diffuse continuous background of scattered radiation appearing in the Laue patterns of diamond [e.g., in figures 5(a) to (k) and in figure 7] is practically suppressed by using thin plates or fine X-ray beams.

8. Influence of high and low temperatures

The spectroscope enables us directly to observe the changes of frequency in the scattered radiations which arise when energy and momentum are exchanged between a beam of light and the crystal which it traverses. The quantum-mechanical character of such scattering is indicated by the difference of the intensities of the radiations of increased and diminished frequencies respectively. The theoretical ratio of these intensities is simply the Boltzmann factor $\exp(-hv^*/kT)$, actual measurements giving values closely agreeing with it. In the parallel X-ray problem, neither the spectroscopic observation of the change of frequency nor the comparison of the intensities of the two components ($\nu \pm \nu^*$) is at present possible. What we observe is the superposed effect of both components of frequency which, as shown in the preceding paper, is proportional to

$$\frac{\exp(-hv^*/kT) + 1}{\exp(-hv^*/kT) - 1} \quad (5)$$

Measurements of the variation of intensity with temperature within the range for which the formula (5) may be expected to be valid should therefore enable us to demonstrate the quantum-mechanical character of the effects and to evaluate the frequency ν^* of the vibrations responsible for them in any particular case.

As shown earlier in this paper, the 1332 vibration is the only one which can be expected to give an appreciable variation of the structure amplitude of the (111) planes in diamond. It follows from this fact and from formula (5) that the intensity of the quantum reflection by the (111) planes should be sensibly independent of temperature. This result was indicated as a consequence of theory in the *Current Science* article of April 1940. In the more detailed paper of May 1940, experiments were described in which the diamond was heated up to 500° C without any notable enhancement of the intensity of the reflection resulting therefrom. Experiments at low temperatures were also indicated as a further test of the theory. A suitable high vacuum low-temperature X-ray camera suitable for quantitative

work was then developed, and the tests made with it with the crystal cooled down to liquid-air temperature showed that the reflections continued to be visible at such temperatures. This was reported in a letter to *Nature*, dated the 20th September 1940 published in its issue of the 23rd November 1940. Further comparisons showed that the intensity of the reflections by the (111) planes at room and at liquid-air temperatures were practically identical. This result was communicated in a letter to *Nature* dated the 23rd November 1940 and published in its issue of the 25th January 1941.

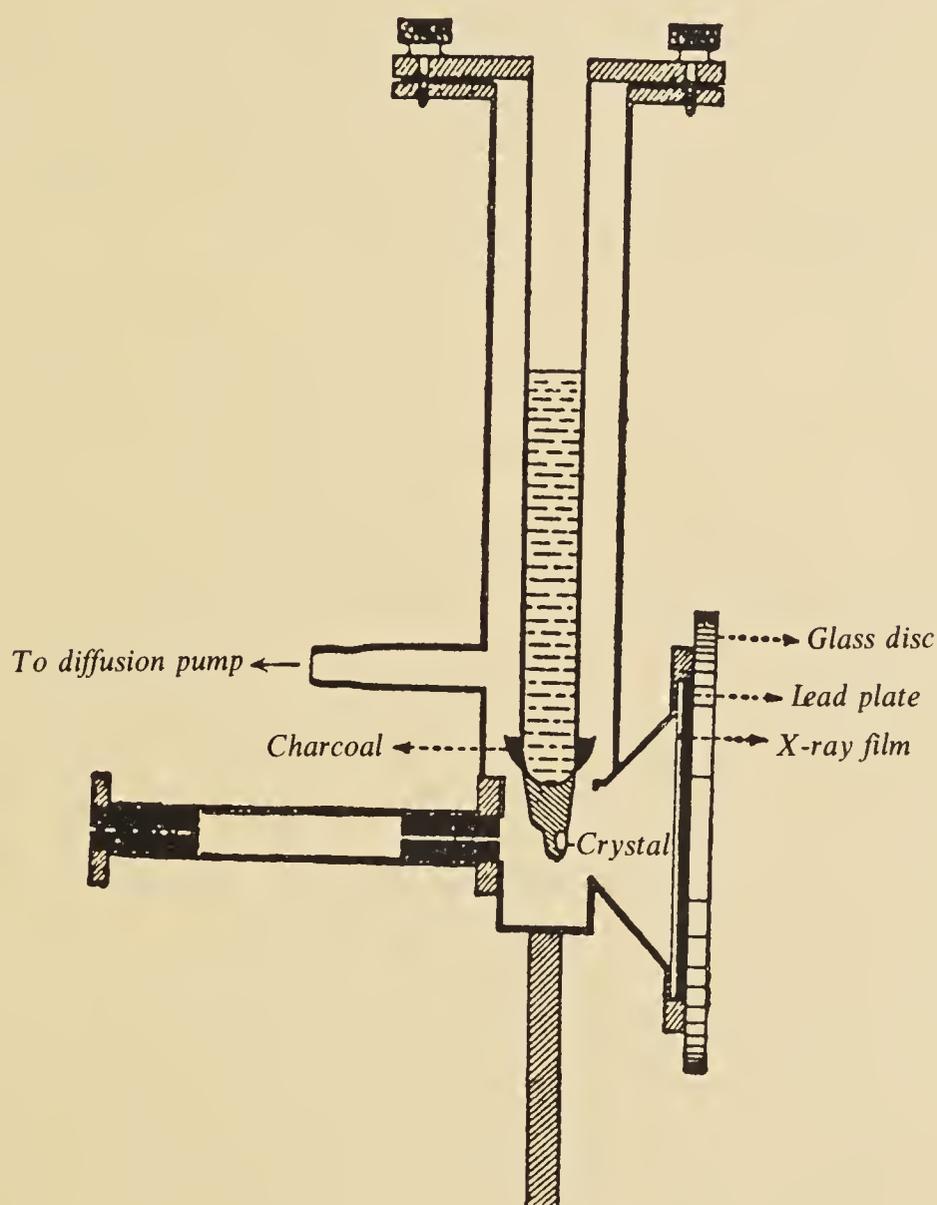


Figure 3. High-vacuum low-temperature X-ray camera.

The special X-ray camera designed and constructed for the experimental study of quantum X-ray reflections at liquid-air temperatures is illustrated in figure 3 above. The diamond is imbedded in a copper block which forms the lowest end of the receptacle for holding the liquid air. A hole bored through the block allows passage for the X-ray beam. Both the crystal and the photographic film recording the X-ray pattern are held inside a high vacuum, the latter being produced by an oil diffusion pump. No intensifying screen was used in these experiments. A small lead disc attached to the film served to cut off the central beam of X-rays.

Photographs were taken under identical conditions with and without cooling the crystal by liquid air. Figures 12(a) and (b) in plate V, reproduce two typical photographs obtained in this way, the former at liquid air and the latter at room temperature. No sensible difference is noticeable in these photographs between the intensities of the quantum reflections appearing in the vicinity of the three Laue spots. Figures 13(a), (b) and (c) in plate V present a similar comparison of the intensities for the quantum reflections photographed under similar conditions at 25° and at 400° Centigrade. Here again, no difference in intensity is perceptible. The experimental results thus completely establish that the (111) reflections arise from a quantum-mechanical excitation of the infra-red vibrations of high frequency. It is important to notice that the reflections seen in figure 12(a) are situated in the near vicinity of the Laue reflections. Accordingly, if the effects had arisen from elastic vibrations of the lattice, these would have been of very low frequency and would therefore have been totally suppressed by the cooling of the crystal to liquid air temperature.

9. Quantum scattering

The diffuse halo surrounding the primary beam is a very striking feature of the Laue pattern reproduced in figure 7, the radiations here used being those of a copper target. Figure 14 in plate VI reproduces a similar picture taken with the X-rays from a molybdenum target and shows a noticeable contraction of the halo, but not so great as should have resulted if the halo had been due entirely to the monochromatic X-radiations present. That the halo is not due solely or even principally to the scattering of the X-rays by elastic vibrations of *thermal origin* is shown by the fact that it persists at liquid air temperatures as seen in figure 12(a) in plate V. Since the halo is recorded with the diamond inside a high-vacuum camera, it is evident that the effect cannot be due to the diffusion of the X-rays by the air. This is also otherwise clear from the fact, already mentioned, that the use of thin plates of diamond tends to suppress the intensity of the halo in comparison with those of the regular reflections. We are thus obliged to conclude that the halo is a quantum mechanical effect, the X-rays exciting the vibrations of diamond lattice having much lower frequencies than 1332 and somewhat similar characters to the vibrations of an elastic solid. The extent to which the intensity of such scattering would be diminished by lowering the temperature would be greatest for the vibrations of the lowest frequency and least for those of the highest frequency. The intensity of the halo should therefore fall off in the close vicinity of the direct beam, and remain sensibly unaffected in directions far removed from it. The distinct sharpening of the halo at low temperatures noticed on a comparison of figures 12(a) and (b) is probably to be explained in this way. The outermost parts of the halo may reasonably be attributed to a diffuse

scattering of the X-rays by the lattice planes of the crystal in combination with the elastic vibrations of the structure.

10. Summary

The paper presents the experimental evidence furnished by the X-ray studies with diamond which confirms the theoretical ideas and mathematical formulation contained in the two preceding papers. The nature of the vibrations of the crystal lattice of diamond is first discussed with special reference to the mode having a frequency of 1332 wave-numbers. This vibration gives a large variation of the structure amplitude of the (111) crystal planes, while other vibrations of a different character leave it unaffected. Various experimental tests show that the X-ray reflections of the second kind given by these planes are truly specular or geometric in character. Measurements of the geometric positions of the reflections over a wide range of crystal settings show a complete agreement with the theoretical formula, the phase-waves of the vibrations appearing parallel to the (100) planes of the crystal. Symmetry demands that there should be three such sets of phase-waves, and this is fully substantiated by the experimental facts. The quantum reflection moves out of the plane of incidence when the crystal plate is rotated in azimuth. The appearance of multiple spots and streamers is also explained by the theory. The intensity of the reflections is of the order of magnitude indicated by the theory and is sensibly independent of the temperature in agreement with it. The phenomenon of quantum scattering is also briefly described and discussed.

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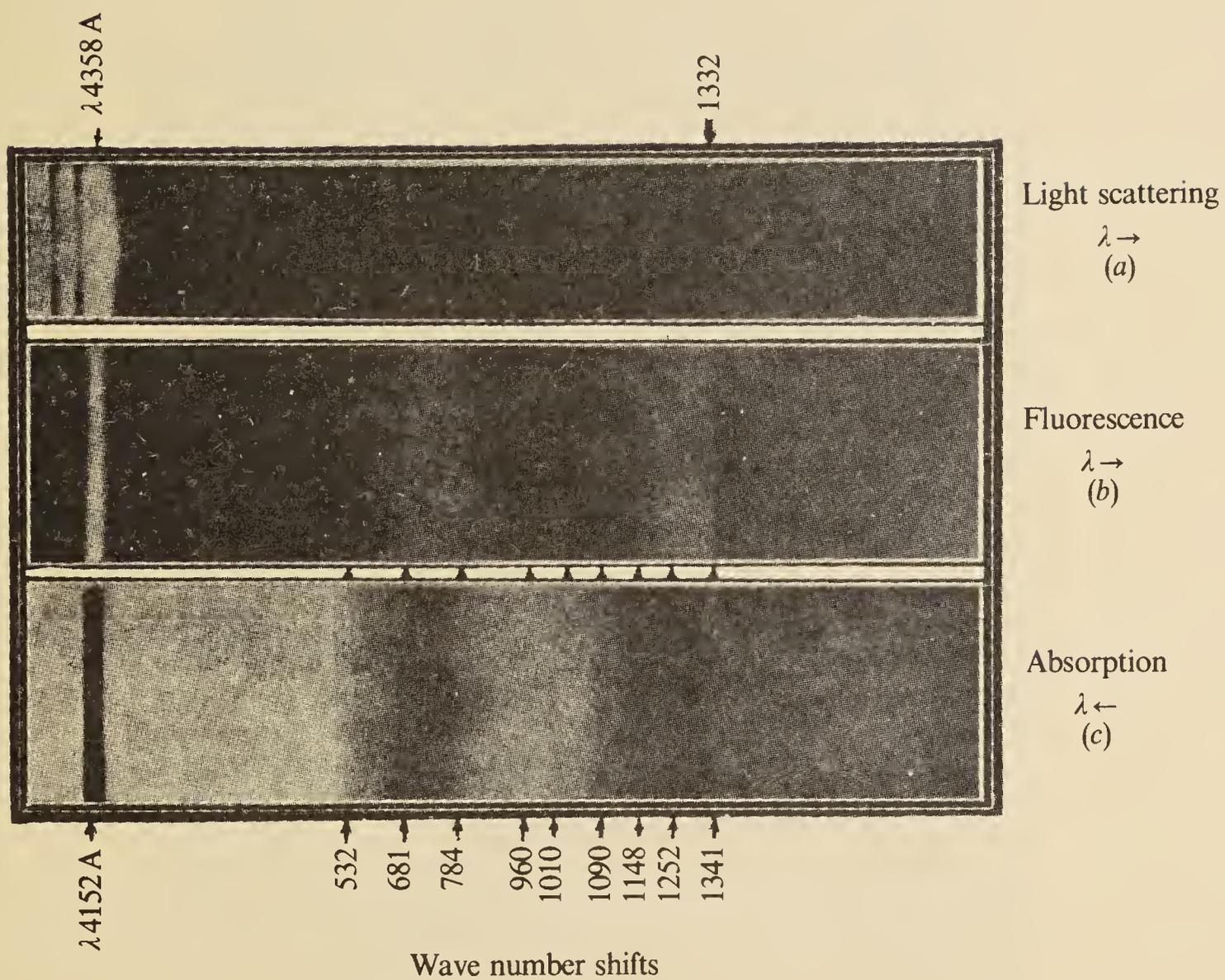


Figure 4. Lattice spectrum of diamond appearing in (a) light scattering, (b) fluorescence, and (c) absorption.

Plate I

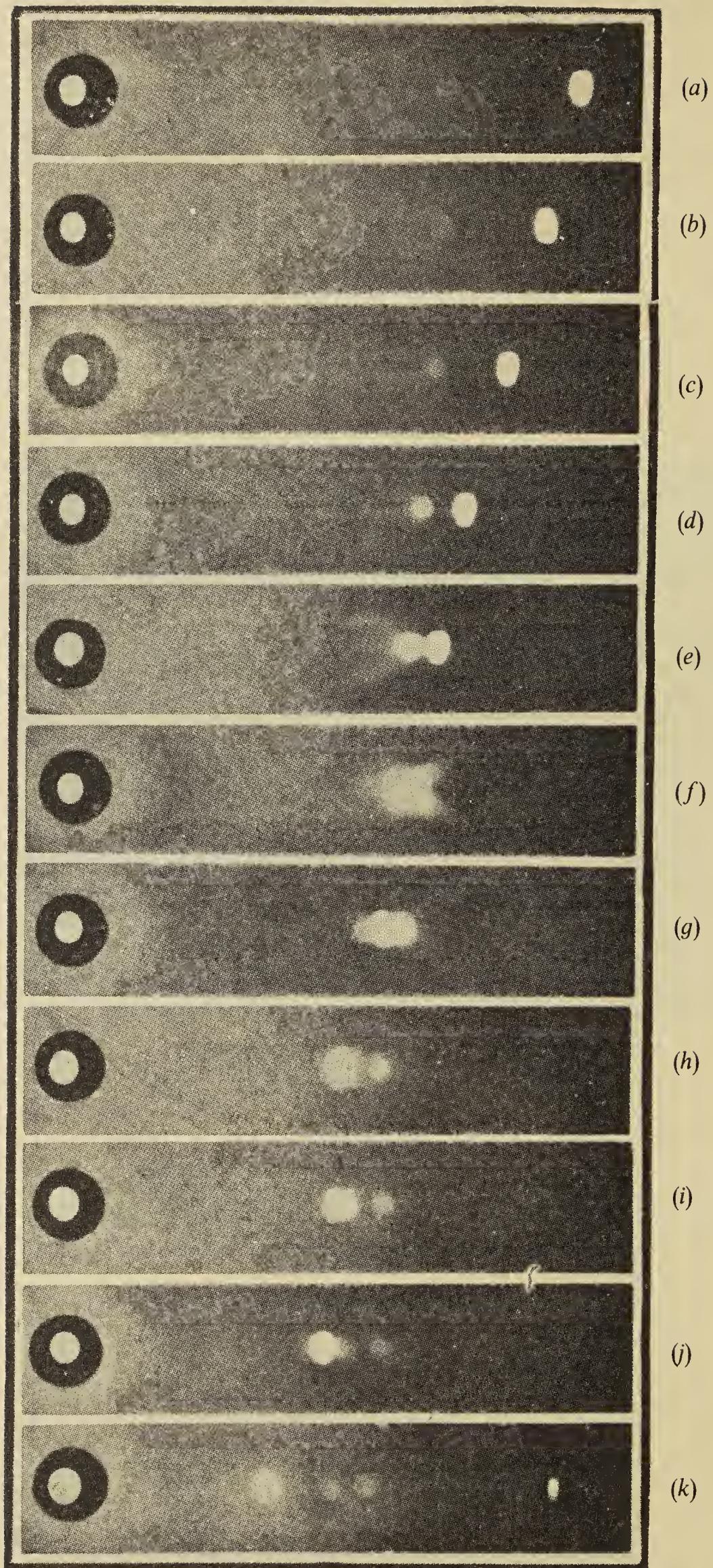


Figure 5. Sequence of changes in (111) reflections with alteration of crystal setting.

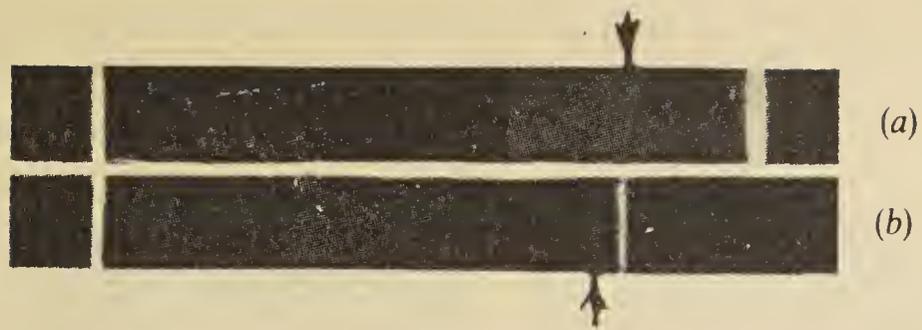


Figure 6. Sharpness of quantum reflection.

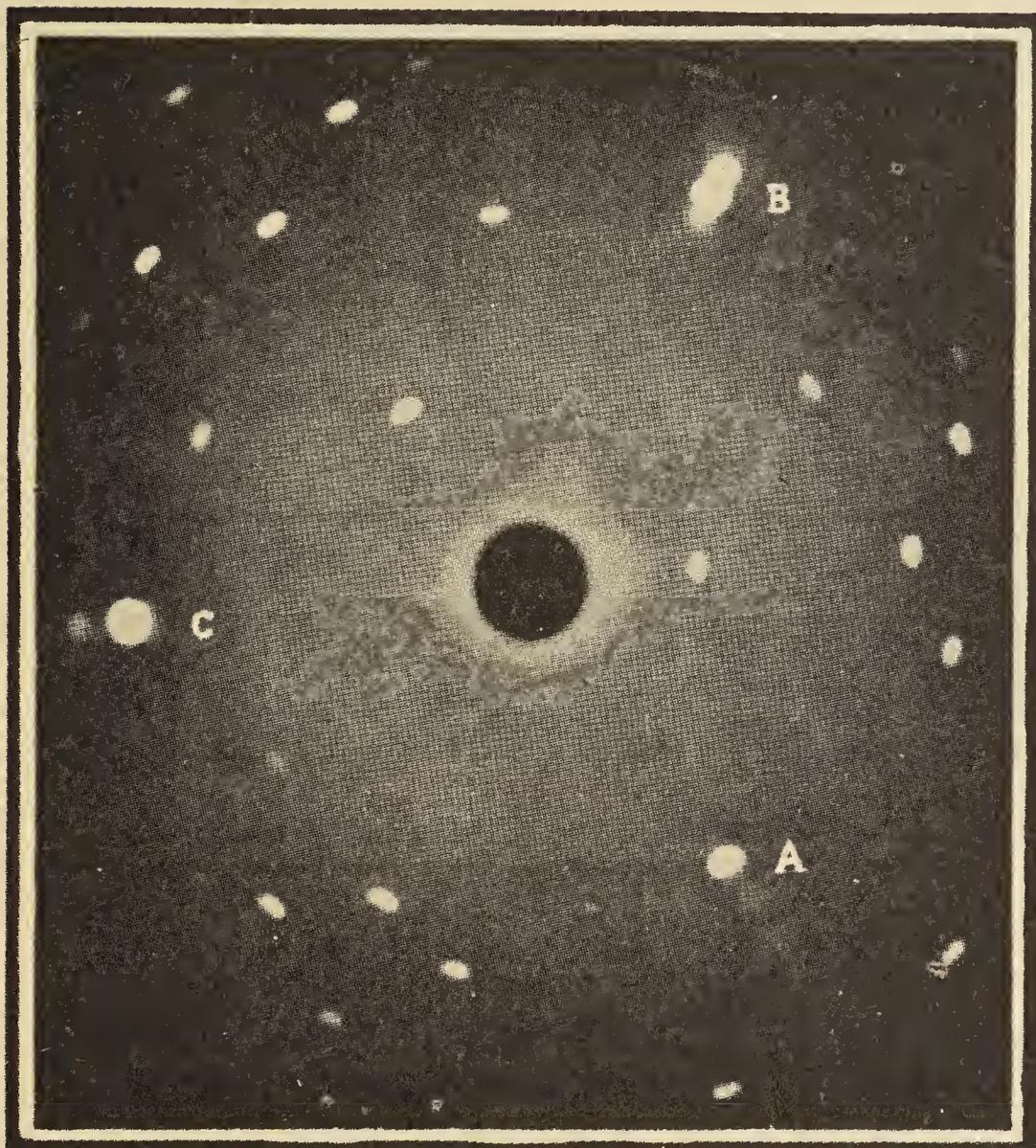


Figure 7. Spots, streamers and halo.



Figure 8. Relative intensities of Laue and quantum reflections.

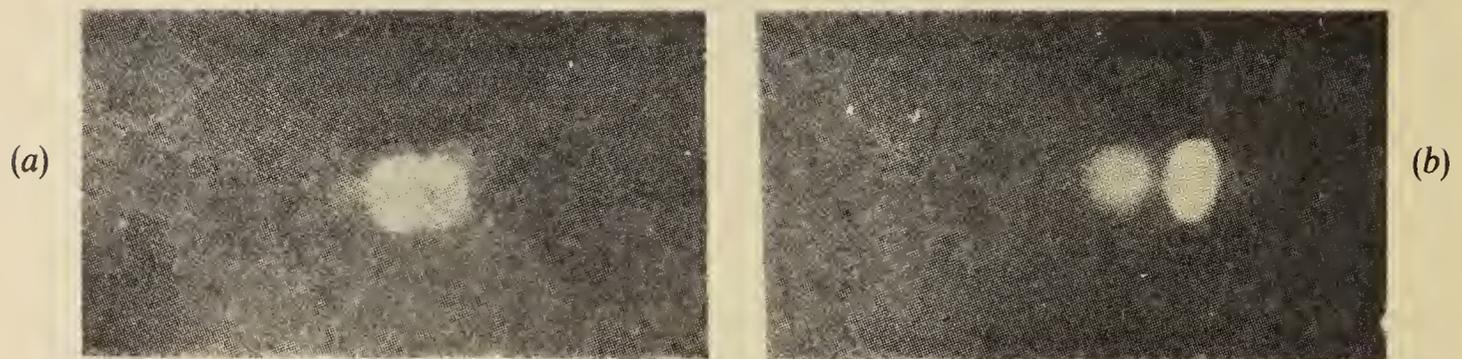


Figure 9. Spots and streamers.

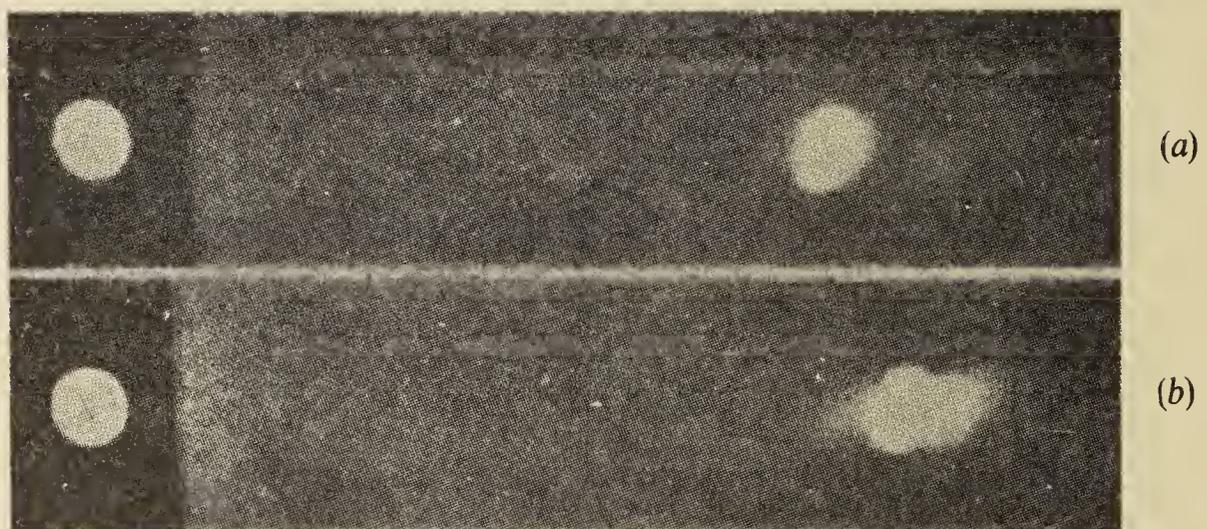


Figure 10. Azimuth effect.

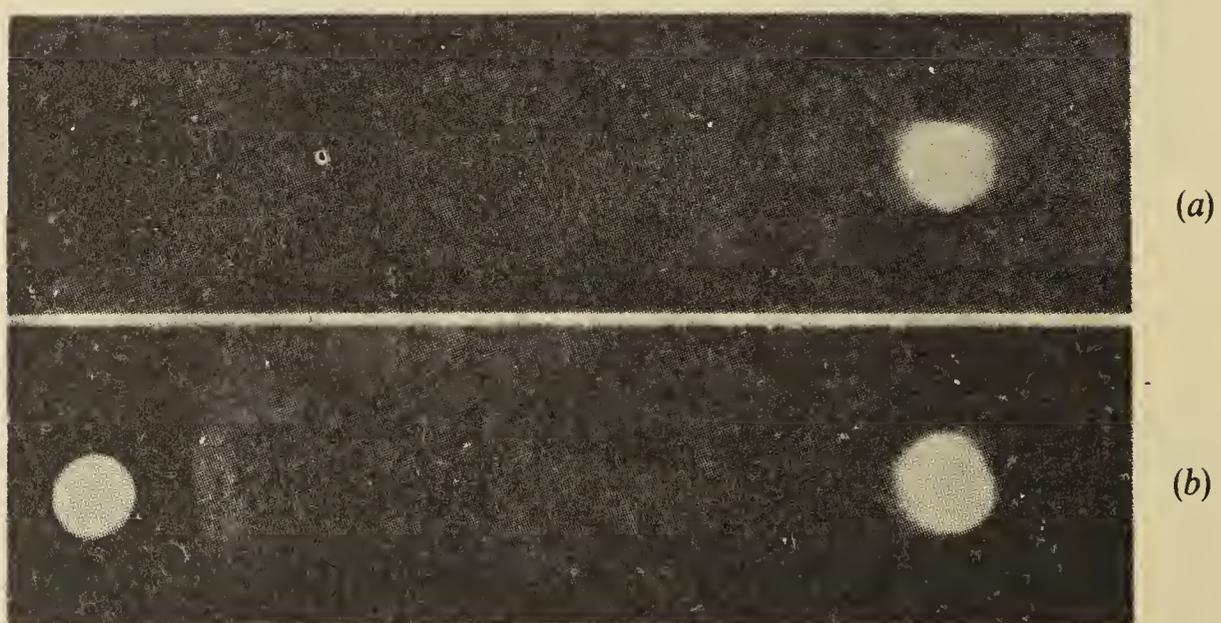


Figure 11. Superposition of classical and quantum reflections.

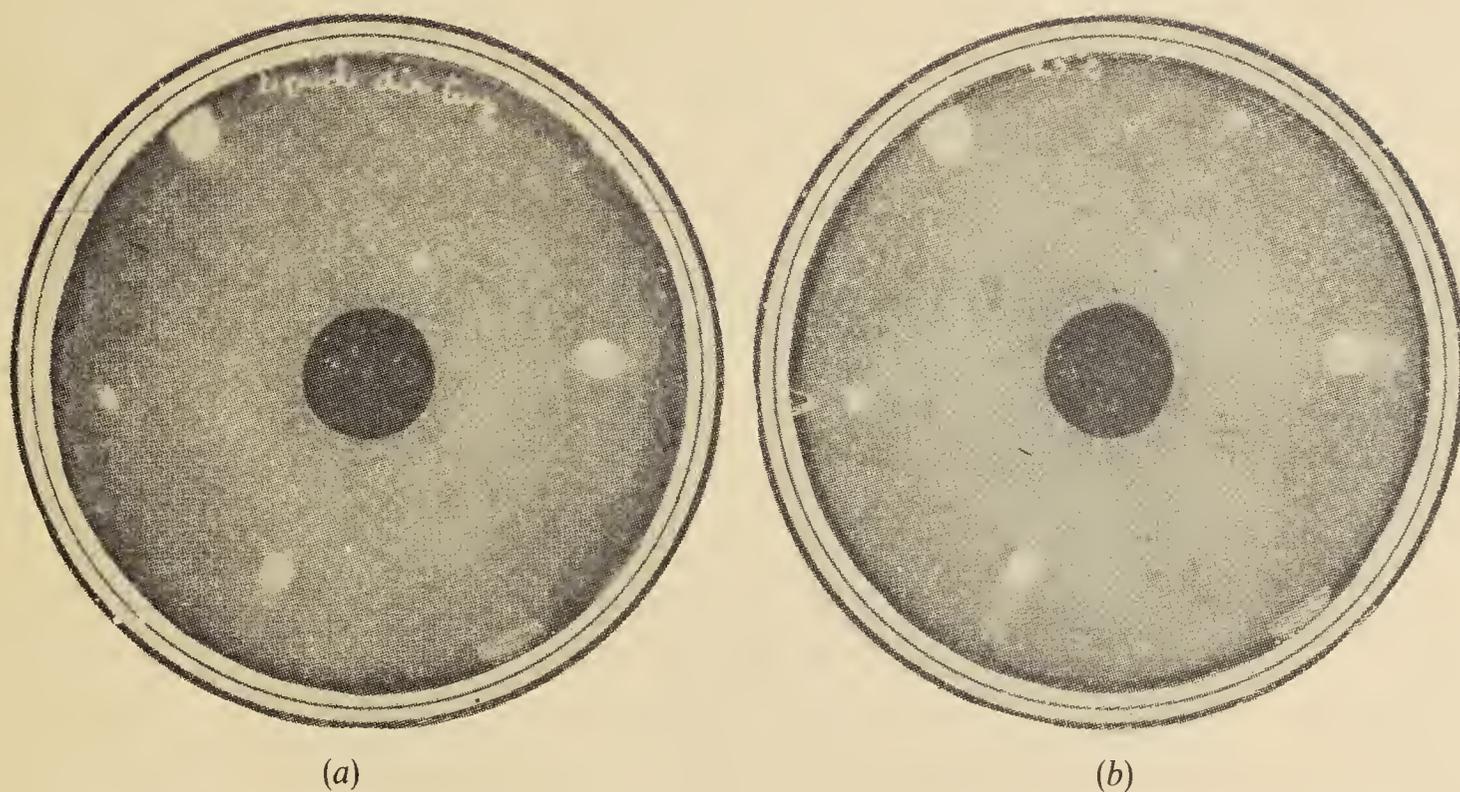


Figure 12. Quantum reflection and quantum scattering at, (a) -180°C , (b) $+25^{\circ}\text{C}$.



Figure 13. Quantum reflections at $+25^{\circ}\text{C}$ and $+400^{\circ}\text{C}$.

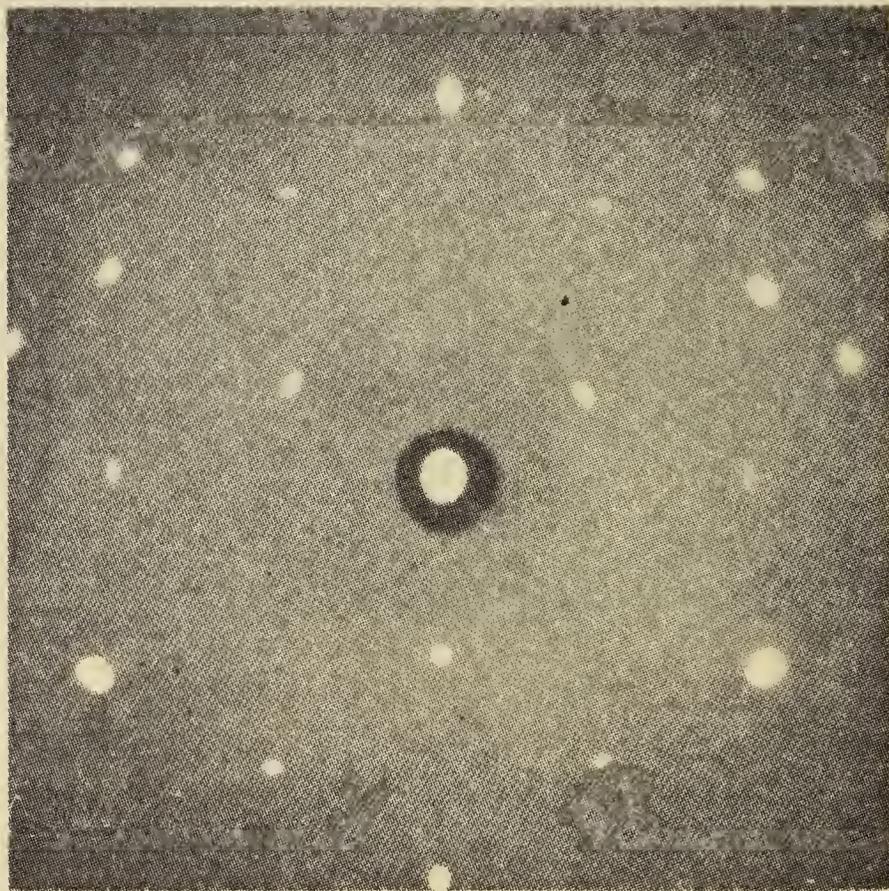


Figure 14. Laue pattern of diamond with molybdenum radiation showing halo.

Plate VI

Dynamic X-ray reflections in crystals*

1. Introduction

Diamond, by reason of its exceptional properties, has played a notable part in the development of our notions concerning the solid state of matter. For instance, when Einstein put forward his famous theory of specific heats, it was the only known solid exhibiting a marked variation of specific heat with temperature, and one may well believe that it was the behaviour of diamond which inspired Einstein to apply quantum theory to the problem. More recent studies on diamond indeed suggest that the properties of this remarkable substance are the pathway to a correct appreciation of the theory of the solid state. That this remark is applicable to the theory of the propagation of X-rays in crystals and of the attendant phenomena forms the major theme of this address.

Diamond has interested the writer ever since 1930, and numerous investigations with it undertaken at his suggestion have appeared in the earlier volumes of the *Indian Journal of Physics* and subsequent to 1933 in the *Proceedings of the Indian Academy of Sciences*. Early in the year 1940, in connection with certain spectroscopic investigations, a few octahedral cleavage plates of diamond were acquired. These formed the beginnings of a collection that has since grown up very considerably. A powerful X-ray set-up was available at the Institute, and Dr P Nilakantan undertook to obtain some Laue patterns with diamond using a copper target as a source of monochromatic X-radiation. The photographs revealed a phenomenon of such a remarkable character and so clearly incapable of explanation on the basis of familiar X-ray theory that the writer had no hesitation in announcing in *Current Science* of April 1940 the discovery of a new X-ray effect, introducing it in the following words: "The new X-ray phenomenon described and illustrated in the present communication has in its physical nature, something in common with both the Laue and the Compton effects: it is a specular reflection of X-rays by crystals but with a change of frequency explicable only on quantum-mechanical principles." The article went on to suggest that the observed reflections had their origin in the excitation of the eigenvibrations of the diamond structure by the incident X-radiations. It was also pointed out that in view of the known high frequency of these eigenvibrations, the thermal agitation

*Jubilee Address to the South Indian Science Association delivered by Sir C V Raman at Bangalore, on the 25th March 1948.

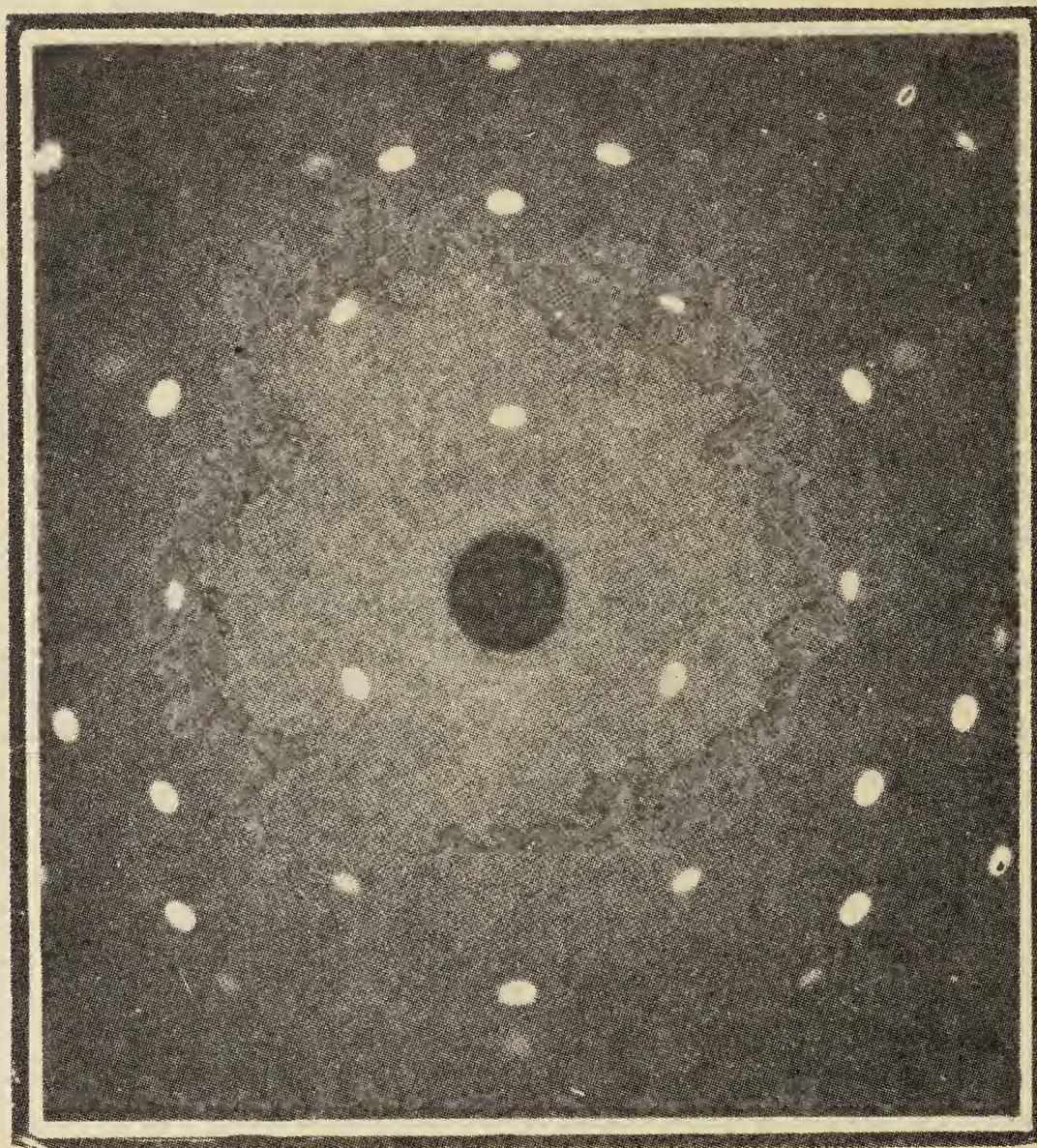


Figure 1. Dynamic X-ray reflections by diamond. CuK_α radiation (after Raman and Nilakantan April 1940).

in the crystal could not be the operative cause of the reflections. Subsequent investigations showed that their intensity was not notably influenced by heating the crystal or cooling it down to liquid-air temperature, thereby confirming the quantum-mechanical nature of the effect. Using fine slits with correspondingly long exposures, the reflections were found to be extremely sharp, thus precluding any explanation of them as due to the thermal X-ray scattering. The appearance of the reflections at various settings of the crystal was explained in the *Current Science* article on the basis of certain considerations regarding the phases of the excited vibrations. These considerations and the formula for the geometric law of the quantum reflection derived therefrom were confirmed with all desirable precision by exact measurements.

The new ideas and principles emerging from the case of diamond naturally suggested a series of investigations with other crystals. The results were published in a series of seven papers in the *Proceedings of the Indian Academy of Sciences* between May and November 1940, and finally in a symposium of fifteen papers under the general title of the "Quantum theory of X-ray reflection" as the October 1941 issue of the *Proceedings*. The subject was then laid aside. It appears

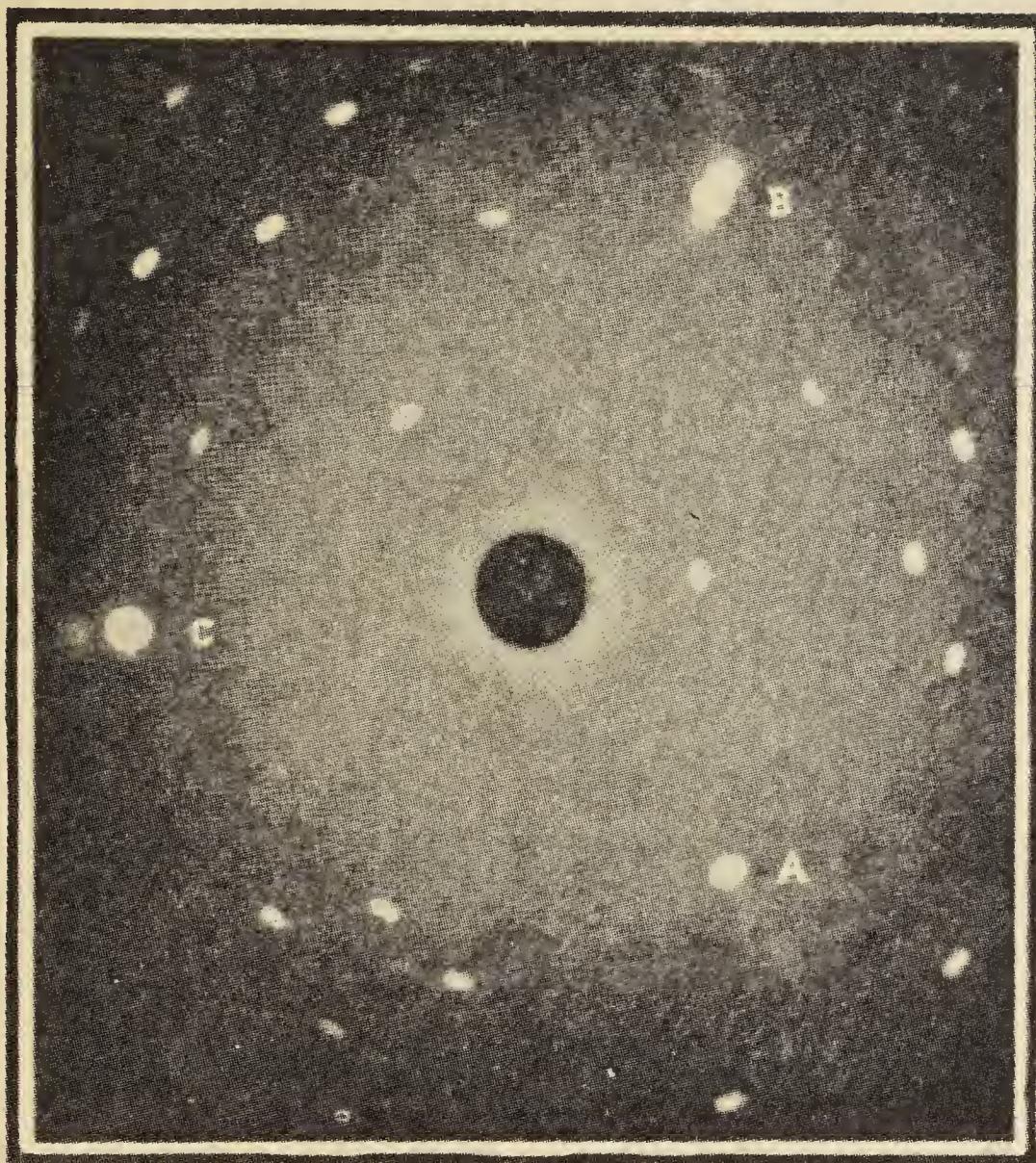


Figure 2. Dynamic X-ray reflections by diamond. CuK_α and K_β radiations (after Raman and Nilakantan, April 1940).

opportune now to return to it, and that some years have elapsed in the interval has not been altogether a disadvantage. For, the studies on several allied topics made at Bangalore during these seven years have cleared the ground for a proper understanding of crystal physics generally and of X-ray physics in particular. Most of the criticisms of the Bangalore publications which were put forward at the time by different writers are seen in the light of the later developments to be without substance or justification.

2. The thermal scattering of X-rays

In considering the phenomena attending the passage of X-rays through a crystal and resulting from the movements of the atoms in it (due to the thermal agitation or other cause), it is desirable in the first instance to fix our attention on such of these movements as can be identified with the elastic vibrations of the solid. There would be an immense number of such movements or normal vibrations possible. Each of these modes extends through the entire volume of the crystal and has a

distinctive frequency and a characteristic pattern of nodal surfaces, the phase of the motion being opposite in every pair of adjacent cells of the pattern. The configuration of the nodal pattern would be determined by several factors, viz., the size of the crystal, its form and the external boundary conditions, the elastic constants and their variation with direction, and it would also be different for each different mode with its particular frequency. It would not be easy—even if it were theoretically possible—to determine the pattern even for a single one of the modes, much less for all of the immense number which need to be considered. We notice, however, that all the factors which are determinative of the nodal pattern are of a *macroscopic* character. Hence, we are justified in inferring that in no case would the nodal pattern bear any particular or specifiable relation to the atomic architecture of the crystal, under which term we refer to the position of the atomic layers and of the individual atoms. The situation here depicted is seen to have important consequences when we proceed to consider the optical aspects of the problem. Fixing our attention on a particular mode of elastic vibration of frequency ν^* , we note that each atom in the track of the X-ray beam can be regarded as a source of secondary radiations of frequency ν , $\nu + \nu^*$, and $\nu - \nu^*$, ν being the frequency of the incident X-radiation. The strength of the radiations of frequencies $(\nu \pm \nu^*)$ would be determined by the amplitude of oscillation of the atoms, while the phases of the scattered radiations as received at any point would be determined by the optical paths and *by the phase of the oscillation of the atom*. Since the latter phase is reversed whenever we pass from one side to the other of each nodal surface in the elastic vibration, it follows that the phases of the scattered radiations would be reversed at the same time. Hence, in the final summation over all the atoms in the track of the X-ray beam, the radiations from the atoms included in the successive cells of the nodal pattern would tend to cancel out by interference. Any resultant left over would arise from the varying amplitudes of the vibrations of the atoms and the varying density of their distribution; but since these variations are uncorrelated, the net result would be unpredictable for any particular ν^* and would also be different for each different ν^* .

We thus arrive at the conclusion that the scattered radiations from the atoms arising from the elastic vibrations in the solid cannot possibly conspire to build up anything in the nature of a diffraction pattern having a recognizable relationship to the atomic structure of the crystal. That a contrary conclusion has been reached by various writers is evidently due to the erroneous nature of the premises on which they have proceeded to consider the problem. We may remark in this connection that in the case of a finite crystal, it is not permissible to postulate the propagation of plane elastic waves in various directions and to consider the optical results of each such wave *independently*. The proper analysis of the elastic vibration is into a set of normal vibrations, each with its own pattern of nodal surfaces determined by the form of the crystal and other factors as stated above.

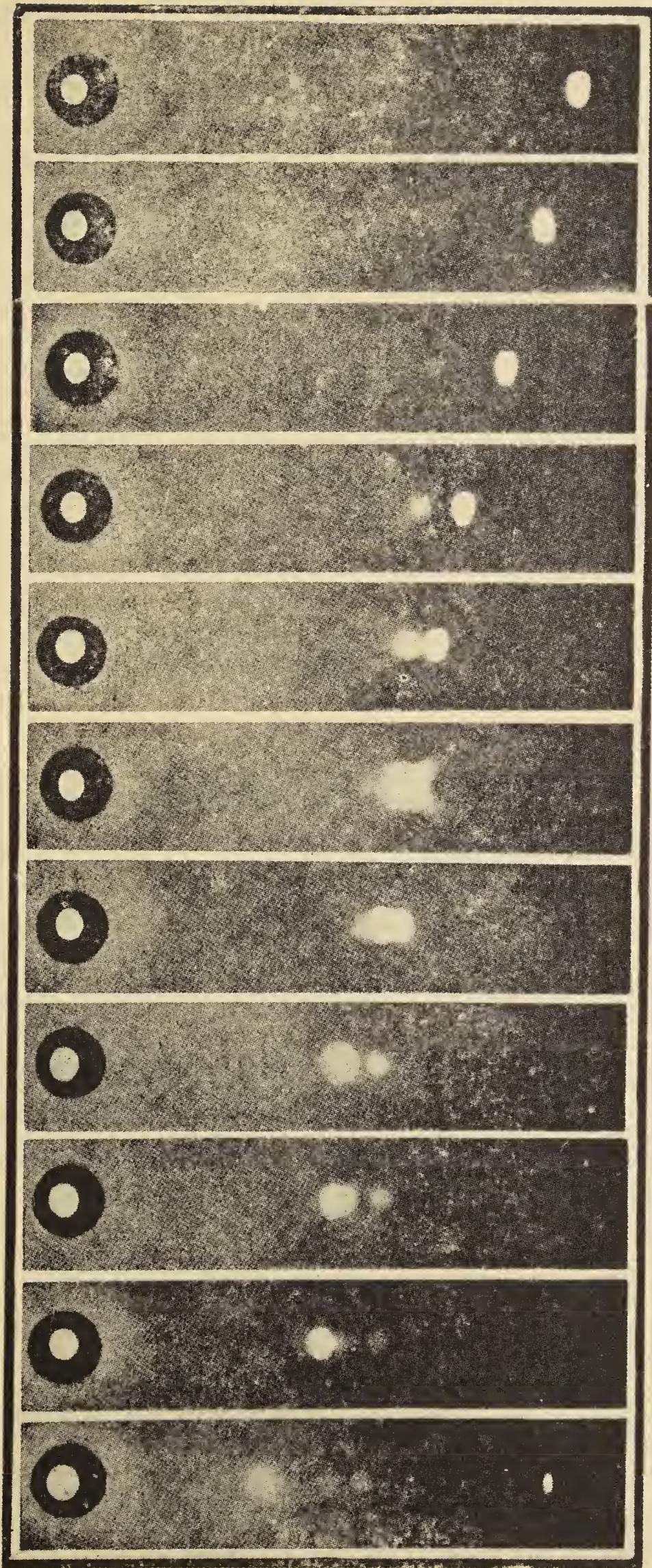


Figure 3. Sequence of changes in (111) reflections by diamond with alteration of crystal setting (after Raman and Nilakantan, November 1940).

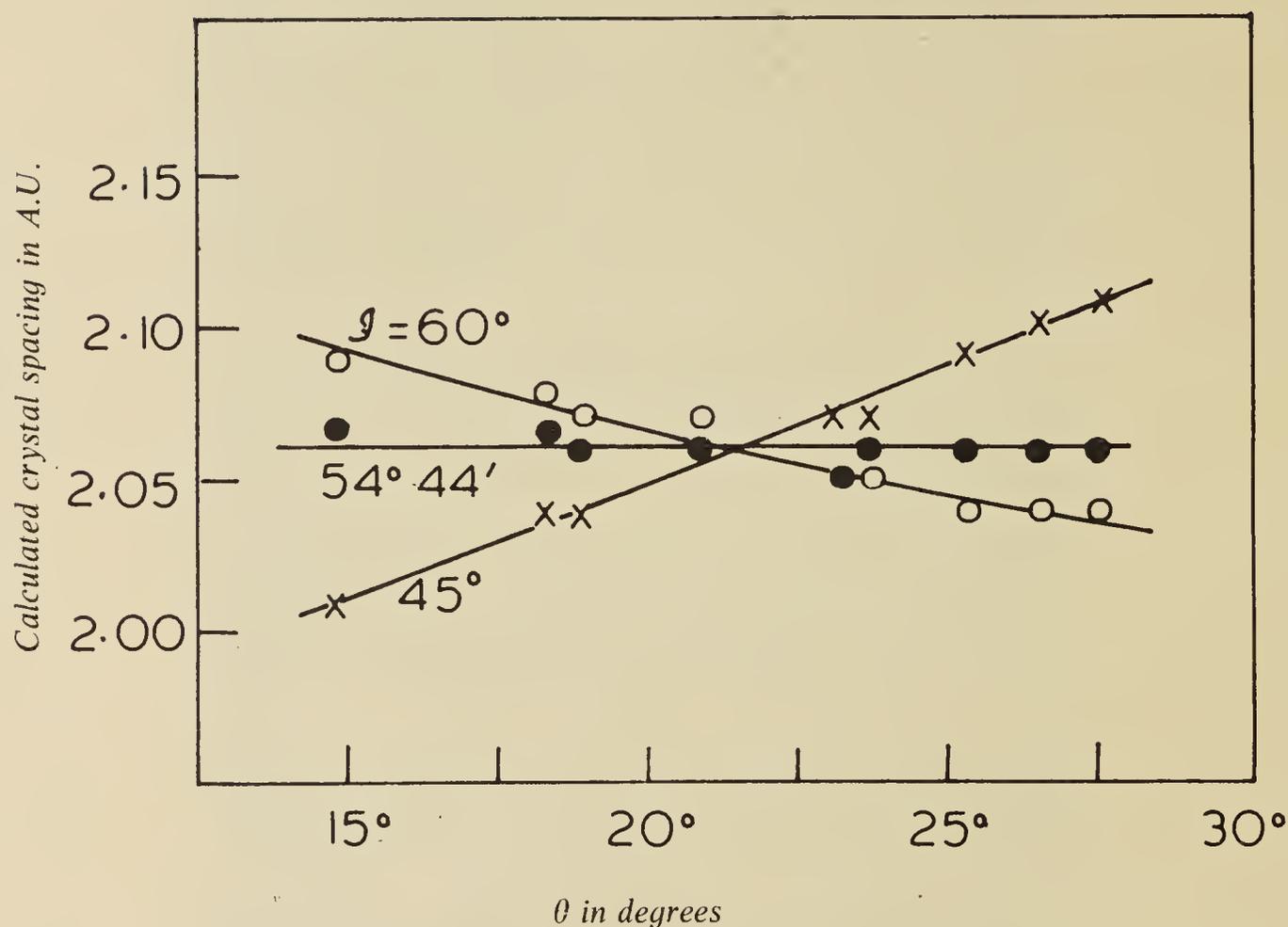


Figure 4. Coincidence of phase waves in diamond with cubic planes (after Raman and Nilakantan, November 1940).

3. The origin of the extra spots

The foregoing remarks make it evident that it is not possible to explain the so-called "diffuse" spots in the Laue pattern of crystals other than diamond on the basis of the elastic vibrations excited in them by thermal agitation or otherwise. This is obvious in the case of diamond by virtue of the observed sharpness or specular character of its extra reflections, but it is equally true for all crystals. In other words, the phenomena exhibited by diamond are exceptional only in the sense that all the properties of diamond are exceptional, viz., they stand out so clearly as to leave little room for being misunderstood. The criticisms of the Bangalore work put forward by various writers who have sought to brush aside the facts observed with diamond on the basis of *ad hoc* explanations or by writing them down as "secondary" phenomena, are thus clearly misconceived.

In the Laue pattern of an octahedral cleavage plate of diamond obtained when the X-ray beam is parallel to a trigonal axis, the extra spots appear symmetrically placed about that axis, and are readily recognized as specular reflections by the (111) spacings of the incident monochromatic radiation, analogous to the ordinary or static X-ray reflections, but obeying a different geometrical law. It follows that the atomic movements in the crystal which give rise to them are related to the structure of the crystal in a precisely definable manner, instead of

being entirely uncorrelated with them as in the case of the elastic vibrations. As we have seen, the incapacity of the elastic modes of vibration to give rise to such effects arises from the fact that they are determined by *macroscopic* factors, including especially the existence of an external boundary and the conditions there subsisting. Even in the purely conceptual case of an infinite crystal where the elastic disturbances can be considered as waves, different wavelengths and directions of propagation can co-exist, thereby precluding the possibility of giving rise to sharply defined "extra" spots. For the same reason, therefore, the atomic movements in diamond, which give the observed reflections cannot be described as waves whose wavelengths and directions are arbitrary in the same manner as those of elastic waves in an infinite solid. Indeed, the analysis of the positions of the reflections by the (111) planes of diamond as actually observed for various settings shows that the planes of constant phase in the atomic movements are severely restricted in their orientation, being in fact exactly parallel to the (100) planes in the crystal. Which of the three sets of these planes is effective, or whether all of them come into operation depends on the particular setting of the crystal with respect to the incident X-ray beam.

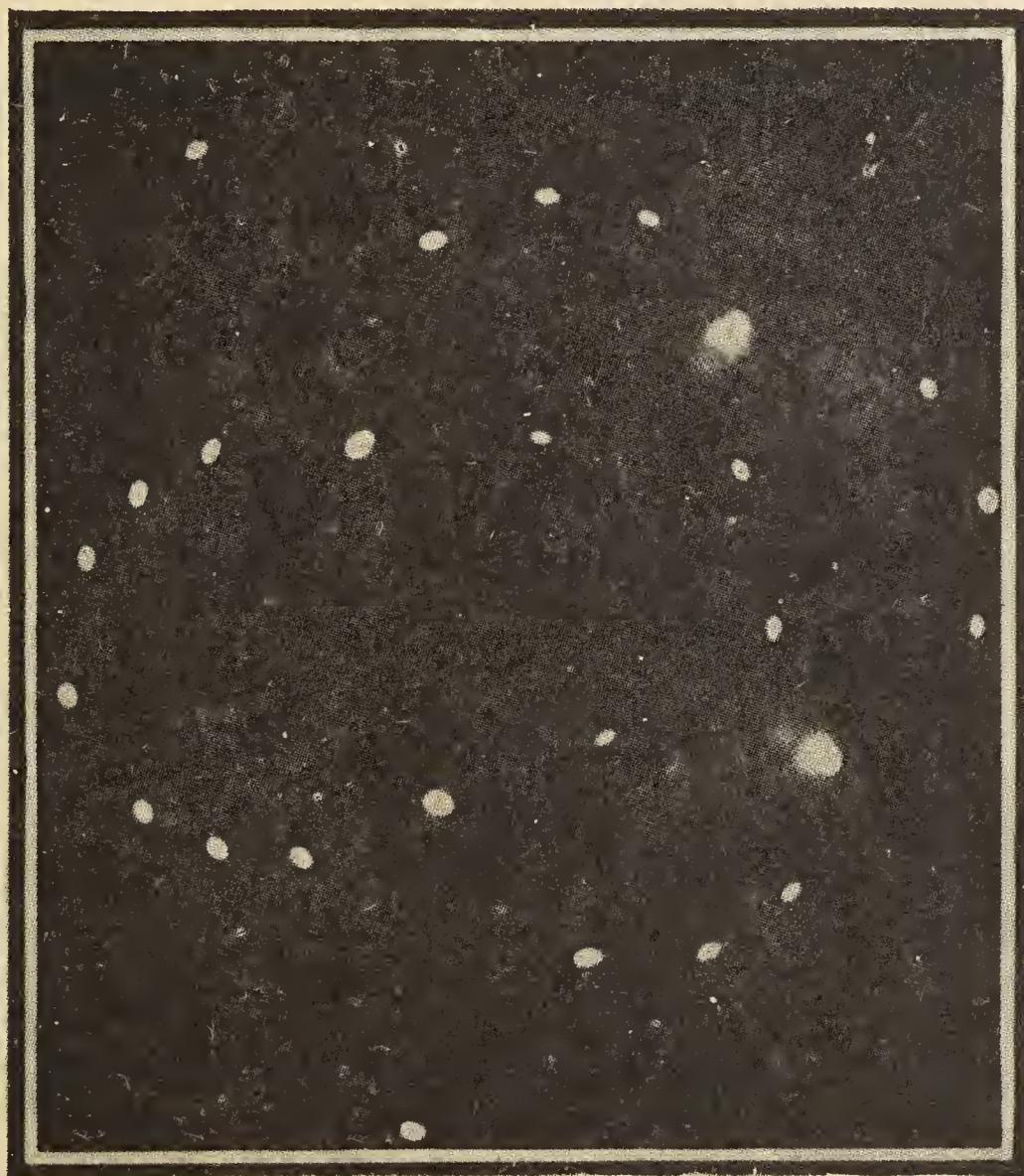


Figure 5. Dynamic reflections by sodium nitrate at 225° C (after Raman and Nilakantan, May 1940).

Thus, alike from theoretical considerations and from the experimental facts, and as in the case of diamond, so also for all other crystals, it is clear that the origin of the "extra" spots has to be sought in types of atomic movement which are precisely related to the structure of the crystal, and which unlike the familiar waves of elastic theory, are uninfluenced by the presence of an external boundary, and whose planes of constant phase are restricted to certain specified orientations. By a simple process of exclusion, we are forced to the conclusion that these movements are the eigenvibrations of the crystal structure which manifest themselves in spectroscopic studies with crystals, and further, that such eigenvibrations possess characters wholly different from the vibrations pictured in the classical theory of elasticity.

4. The eigenvibrations of crystal structure

Our argument thus leads us to recognize the fundamental relationship between the physics of X-ray propagation in crystals and the physics of their spectroscopic behaviour. It also shows that the older views which sought to force the spectroscopic picture of crystal behaviour into a pattern similar to that of its elastic vibrations are fundamentally erroneous. Indeed, the X-ray phenomena observed with diamond compel us to make a fresh approach to the theory and of their relationship to the spectroscopic phenomena. Such an approach has been made in the introductory paper of a symposium on "The dynamics of crystal lattices", published by the *Indian Academy of Sciences* as its *Proceedings* for November 1943. More recently, the spectroscopic consequences of the new theory have been worked out and the results compared with the experimental facts in numerous cases, viz., diamond, magnesium oxide, the alkali halides, etc. The results have been published as a symposium of the eigenvibrations of crystal structures of nineteen papers on "The vibration spectra of crystals" forming the *Proceedings of the Indian Academy of Sciences* for December 1947. The theory is so successful in explaining the facts of observation, including such as are wholly unintelligible on the basis of the older theories, as to leave no room for doubt regarding the essential correctness of the new approach.

The main result of the new theory is that, whereas on the older theories the vibrations both in the acoustic and optical ranges of frequency yield continuous spectra, they appear in the new theory as a set of modes with sharply-defined monochromatic frequencies $(24p-3)$ in number, there being p atoms in the unit cell of the crystal lattice. In $(3p-3)$ of these modes, the vibrations have the same amplitude and phase in adjacent cells of the lattice, while in the remaining $21p$ modes, the amplitude is the same while the phase alternates in successive cells along one, two or all three of the axes of the lattice. The actual number of discrete frequencies would be much less than $(24p-3)$, if the crystal belongs to the higher symmetry classes. In the case of diamond, for instance, the $(3p-3)$ frequencies

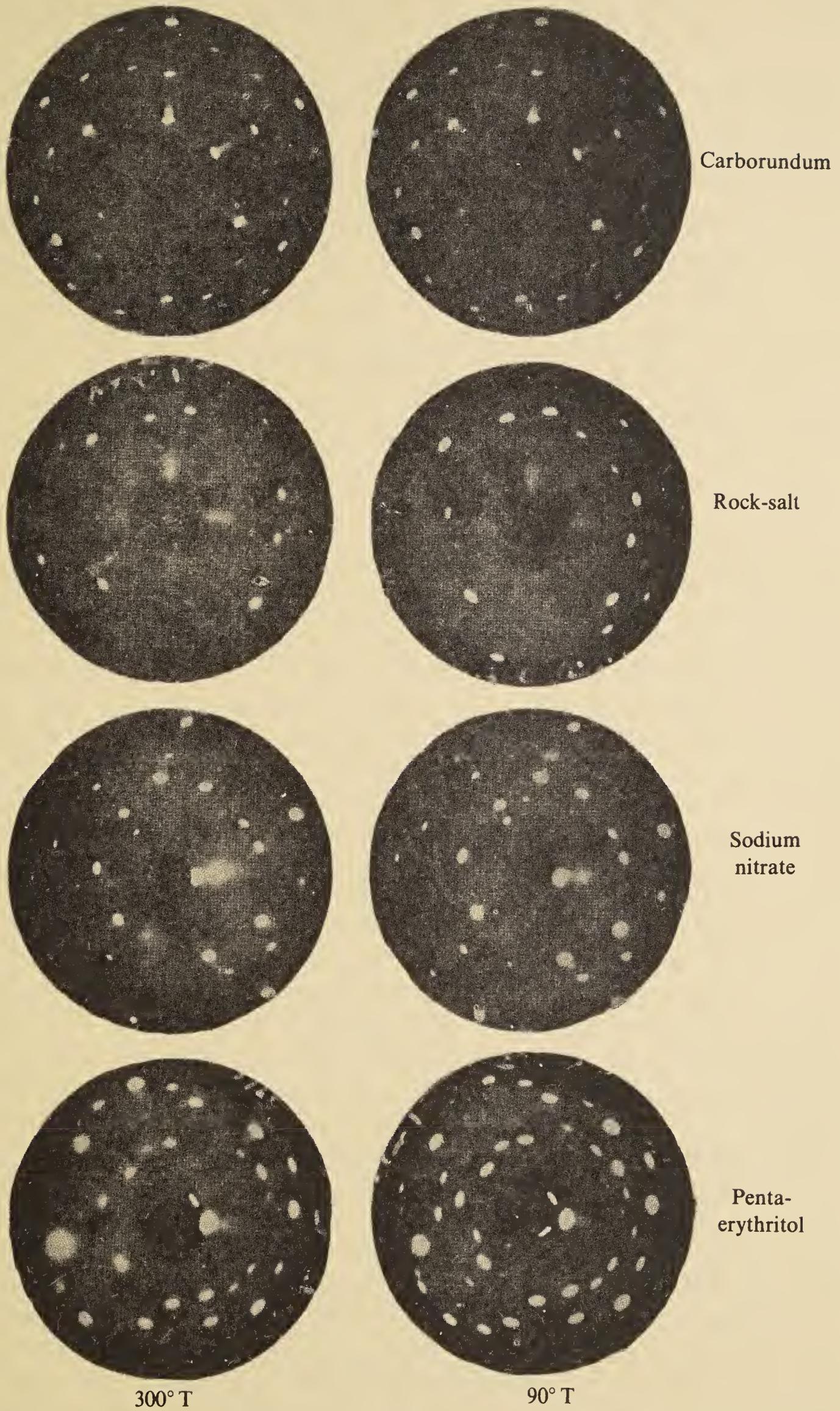


Figure 6. Quantum X-ray reflections by crystals at 30° C (*left*) and -180° C (*right*) (after C S Venkateswaran, September 1941).

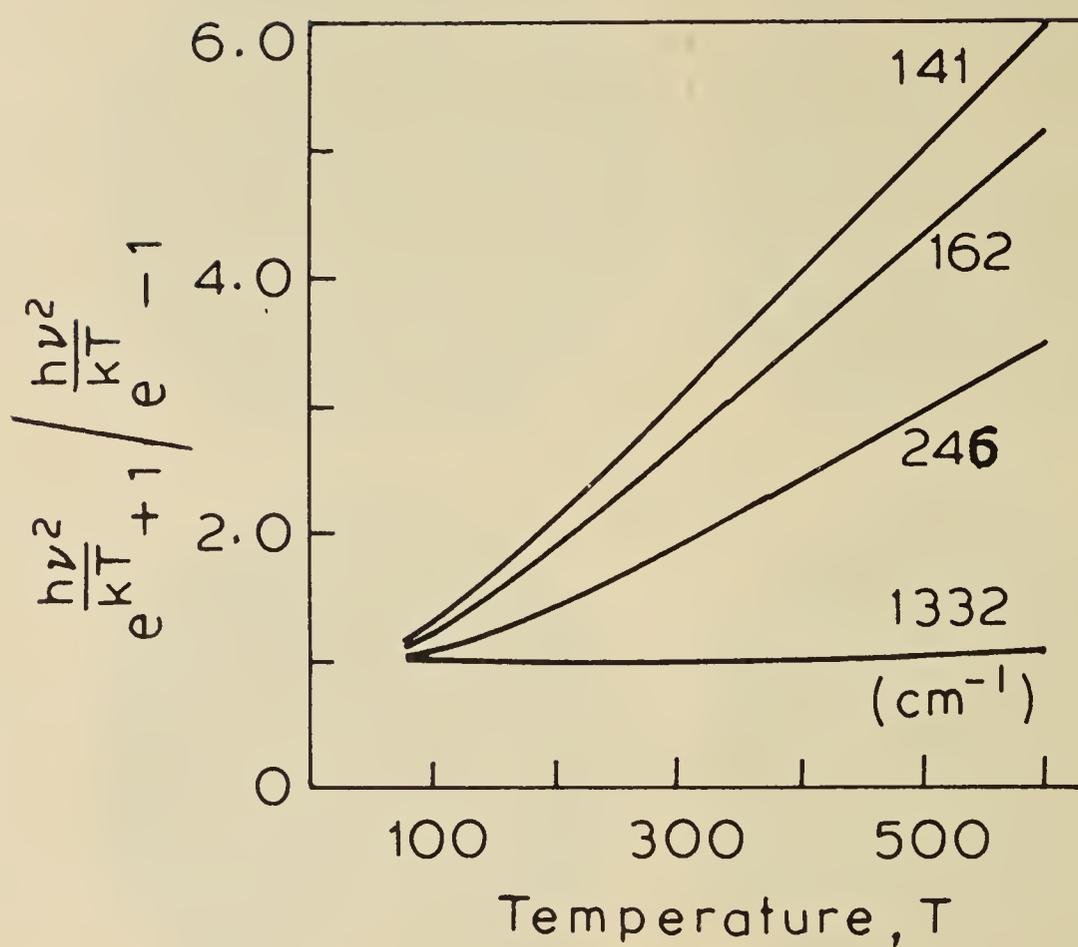


Figure 7. Temperature factor of quantum reflection, theoretical (after Raman, September 1941).

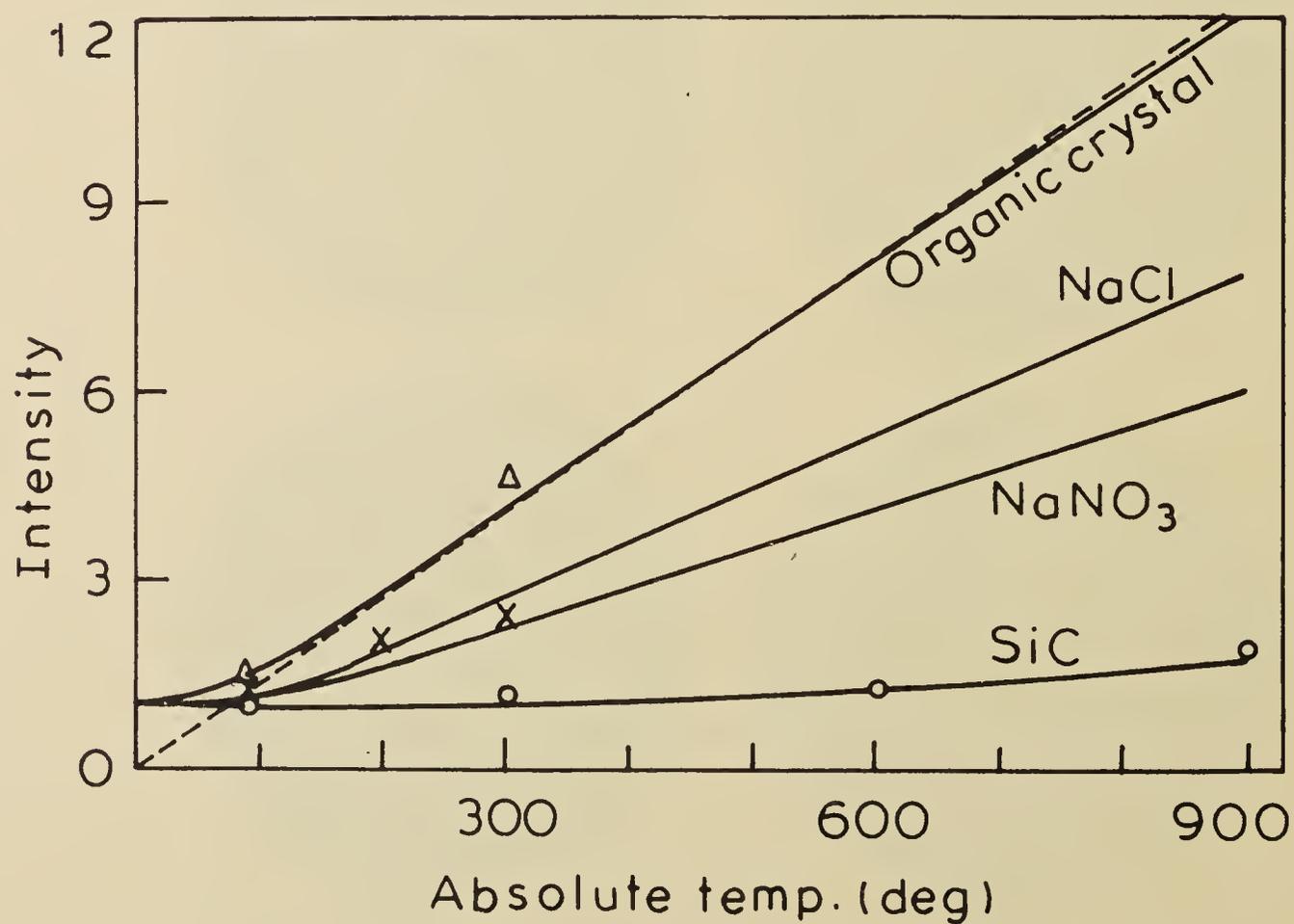


Figure 8. Temperature factor of quantum reflection, experimental (after C S Venkateswaran, September 1941).

reduce to only one, where the $21p$ frequency reduce to seven in number. The vibrations and their respective frequencies may be regarded as characteristic properties of the dynamic unit of the crystal structure which is a super-cell with twice the dimensions and eight times the volume of the unit cell of the lattice. It may be remarked that the 3 excluded degrees of freedom form the residue which goes over into the spectrum of the elastic vibrations of the crystal.

5. Excitation of the eigenvibrations

It is possible to excite the eigenvibrations of a crystal in various ways, the most obvious and universal method being that of thermal agitation which is always effective, provided the temperature is sufficiently high. We have also various optical methods in which the evidence of excitation is furnished by spectroscopic study, e.g., observations of the spectrum of the scattered light, of the absorption in the infra-red, and also in favourable cases of the absorption in the visible spectrum, and of the luminescence spectrum at low temperatures. The monochromatic character of the vibration frequencies comes directly into evidence in all such cases, irrespective of the particular method of excitation adopted, showing thereby that it is a characteristic property of crystal structure and not a consequence of the particular method of excitation employed. The activity of the individual modes may, however, differ in respect of the different methods of excitation. For instance, in the cases of light-scattering and of infra-red absorption, they are complementary and mutually exclusive in respect of the fundamental frequencies in the case of crystals possessing a centre of symmetry. This feature disappears when we consider the overtones and summations of the fundamental frequencies where anharmonicity, mechanical or optical, comes into play. The appearance of overtones and summations with appreciable intensities in the optical methods of excitation indicates that the vibrations excited are highly localised, and that in consequence, the vibration amplitudes are comparable with the interatomic distances. If, on the other hand, the excitation extends over a large volume in the crystal, the energy of a quantum of the particular frequency distributed over such volume would result in the amplitudes being infinitesimal and hence incapable of giving rise to overtones or summations with appreciable intensities. On the other hand, in the excitation which results in dynamic X-ray reflections, we must picture the vibration as occurring in the same phase or with slowly varying phases over an extended volume of the crystal, since otherwise no observable reflection could result. The larger the volume in which the excitation occurs, the more sharply defined would the resulting reflections be. The extreme sharpness of the dynamic reflections in the case of diamond where the bonding between each lattice cell and the next is strong is readily understood on the basis, while the diffuseness of the "extra" spots in weak crystals, such as for instance organic compounds, is also intelligible as a consequence of the weakness

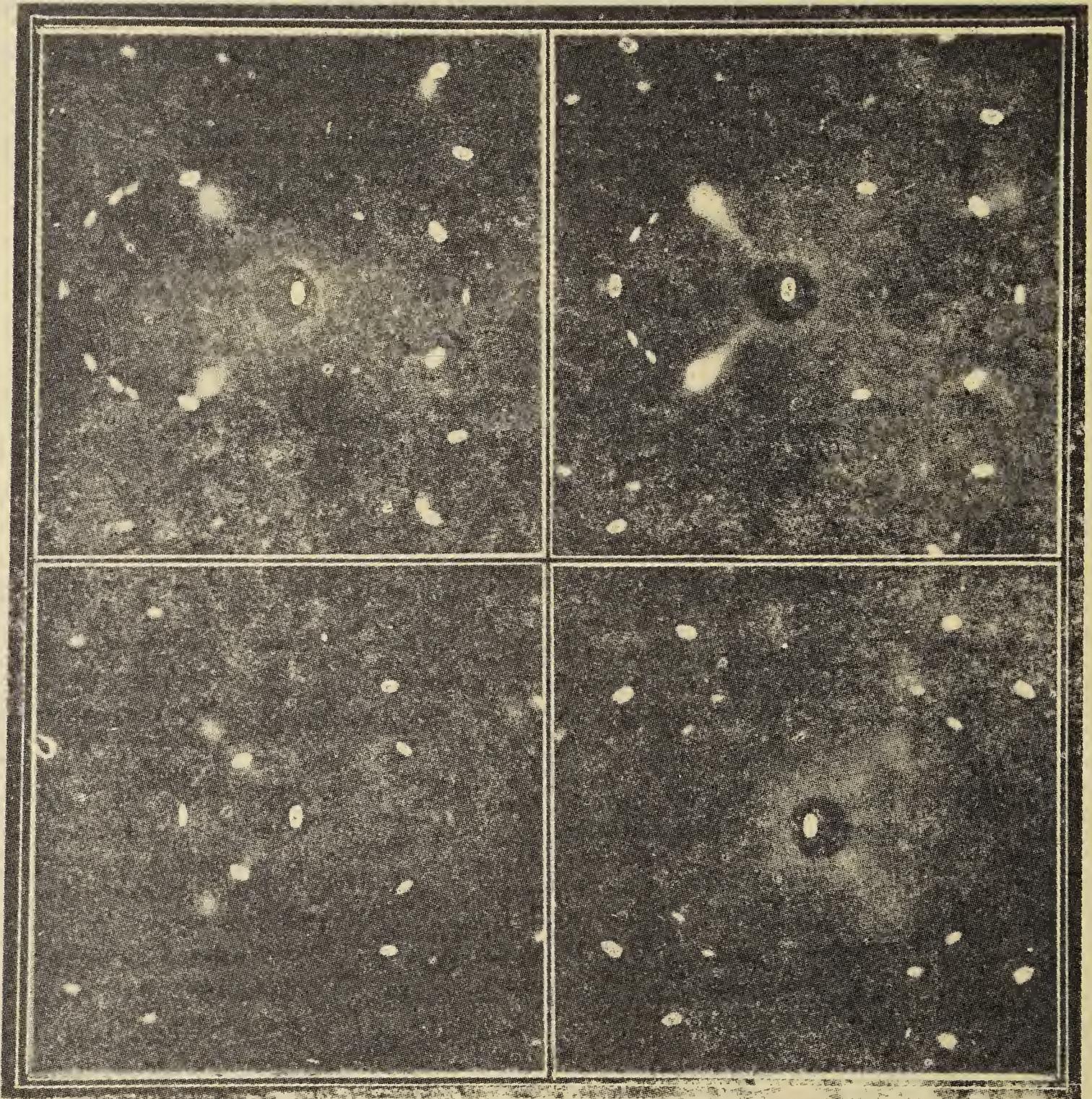


Figure 9. Dynamic X-ray reflections by hexamethyl tetramine (after C S Venkateswaran, October 1941).

of the binding between the successive cells of the structure. It should be remarked that the restriction in the volume of excitation would result in an increase of the amplitude of vibration, and this would exactly set off the decrease in the number of lattice cells which co-operate to give a dynamic reflection. The amplitude of vibration, would also be dependent on the masses and binding forces involved. Hence, it is quite possible for crystals which give only "diffuse" spots nevertheless to exhibit them with notable intensities.

6. Influence of temperature

In many cases, and especially where the binding forces are weak or the atomic masses are large and hence the eigenfrequencies are low, the eigenvibrations would be excited by thermal agitation, and hence such thermally excited eigenvibrations would have to be considered in respect of the X-ray phenomena as well. The theoretical position is somewhat analogous to that arising in the case of the excitation by optical methods, viz., the scattering of light, where we are concerned with both positive and negative shifts of frequency in the spectrum of the diffused light. Instead of the ground state, the thermally excited state of eigenvibration would be the starting point for their excitation by the incident X-radiation, and hence it can occur in either direction, viz., further excitation or a de-excitation. The dynamic reflections arising in either way would appear superposed in the finally observed result, and the net consequence to be theoretically expected would be an increase in the intensity of the reflection with rising temperature, besides subsidiary effects such as increase in diffuseness. The magnitude of the increase in intensity would depend on the frequencies of the eigenvibrations which are effective in giving the observed reflection, and the proportionate increase would be the smaller, the higher the frequency or frequencies under consideration. *Per contra*, the intensity would diminish when the temperature is lowered, but since the quantum-mechanical excitation would persist in every case, the reflection would not disappear even at the lowest

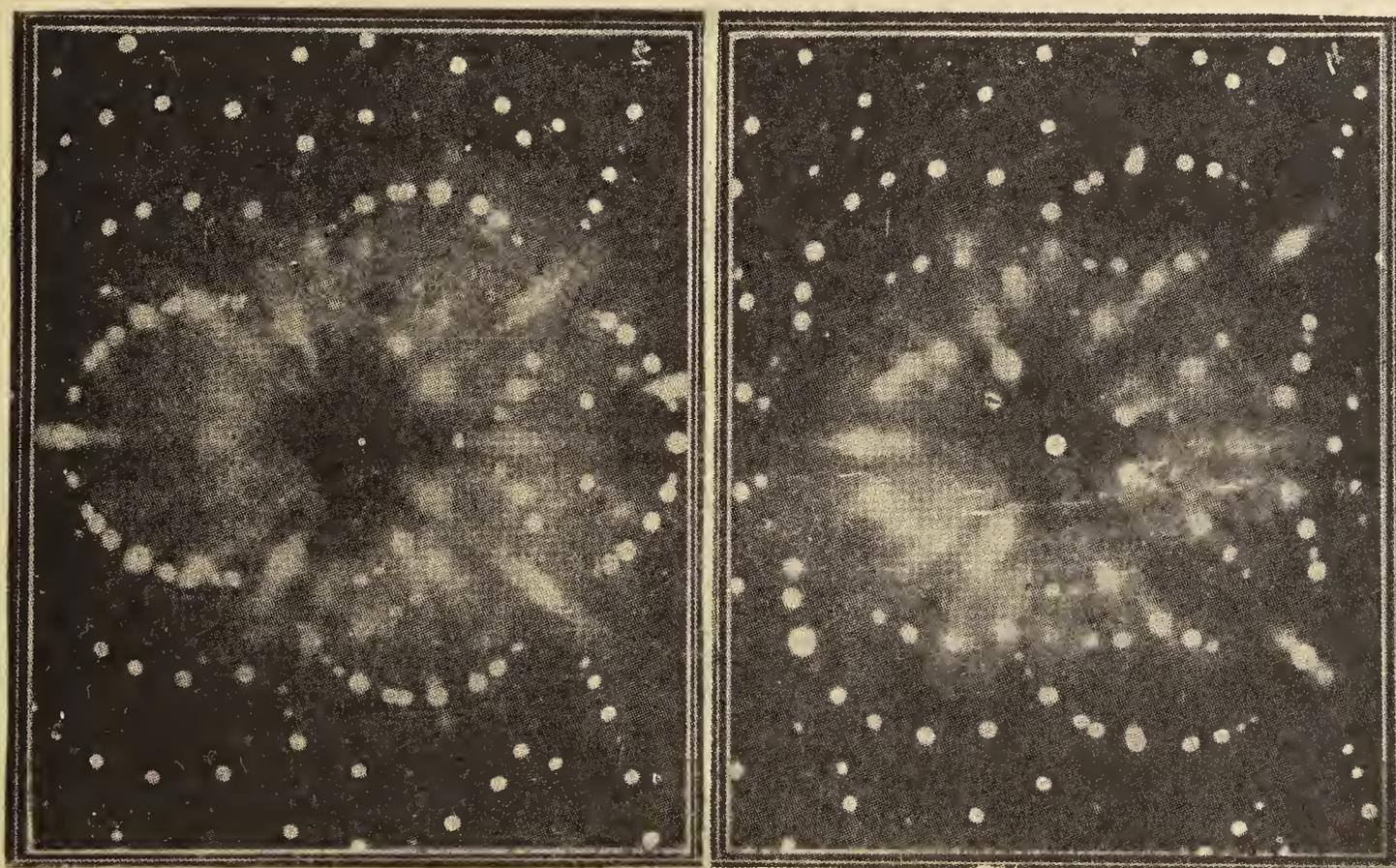


Figure 10. Dynamic X-ray reflections by calcite for different settings (after Nilakantan and Nayar, October 1941).

temperatures but would on the other hand persist. The intensity at low temperatures would be relatively the largest in the case where the eigenvibrations involved would have relatively the highest frequencies. There is no reason to expect any notable dependence of the magnitude of the temperature variation on the setting of the crystal at which the dynamic X-ray reflections are recorded.

7. Dependence on crystal structure

It will be evident from what has been stated above that the pattern of dynamic X-ray reflections by a crystal would be largely determined by the number and nature of its eigenvibrations and their frequencies, and also on the manner in which these eigenvibrations influence the structure-amplitudes of the various crystal planes. Each individual case would have to be considered on its merits as in the case of static X-ray reflections, but general considerations regarding the nature of the oscillations possible in ionic, molecular or layer lattices would enable us to predict or at least understand the general nature of the dynamic X-ray patterns to be expected in these respective cases. But it would take us beyond the scope of the present article to enter into these details.

C V RAMAN

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X-rays and crystals*

SIR C V RAMAN

It is familiar knowledge that every crystal is a three-dimensionally periodic grouping in space of atomic nuclei and electrons held together by their mutual interactions so as to form a rigid solid. We recognise in each crystal a unit of its structure containing, say, a group of p atoms, this group repeating itself at regular intervals along three directions which are designated as the axes of the structure. The atoms in the crystal may accordingly be regarded as consisting of p sets, all the atoms of a particular set being equivalent to each other and located at regular intervals in a space lattice whose axes are those of the crystal.

2. Diffraction of X-rays by crystals

That the geometric picture of crystal architecture briefly indicated above is not just a mathematical hypothesis but a physical reality was first demonstrated by the famous experiment of Laue and his collaborators. When a narrow pencil of X-rays traverses a crystal and is received on a photographic film held behind it, a pattern of spots surrounding the impress of the incident beam appears on the film when developed. It is well recognised that these Laue spots—as they are called—represents monochromatised reflections of the incident X-ray beam by the stratifications of the electron density parallel to the various crystallographic planes in the structure of the crystal. The intensity of each spot is indicative of the magnitude of the corresponding periodic variations of electron density normal to the planes under consideration. The theory of the Laue experiment can be dealt with in a purely classical manner by attributing a certain scattering power to each volume element in the electron cloud present in the crystal proportional to its local density. This scattering power derives from the fact that the electrons would be set in motion and oscillate with the same frequency as that of the electromagnetic field which the incident X-ray beam represents. On this basis, the scattered radiations from all the volume elements would have the same frequency as the incident X-rays, as also specific phase relationships determined by their

*Presidential Address to the Indian Academy of Sciences at the Hyderabad Meeting on 27th December, 1955.

relative positions. The scattered radiations therefore would be capable of reinforcing each other's effects in certain specific directions determined by the wavelength of the X-rays and the spacing of the stratifications, in accordance with recognised optical principles. Concentrations of intensity accordingly appear in the directions representing a highly restricted selection of wavelengths from the incident white X-radiation.

3. Atomic nuclei and X-ray diffraction

The foregoing picture is obviously however an over-simplification. It implicitly assumes that the electrons which scatter the X-rays remain firmly bound to the structure of the crystal and that the latter also remains otherwise unaffected by the passage of the X-ray beam. The strength of the binding of the electrons to the atomic nucleus or nuclei closest to them necessarily enters into the picture and would influence the intensity and phase of the scattered radiations to an extent determined by the approach of the frequency of the incident X-radiation to the characteristic X-ray absorption frequencies of the electrons. Indeed, recent X-ray researches have shown that these factors have to be taken into account in the theory of X-ray diffraction by crystals.

The foregoing remarks indicate that considerations somewhat analogous to those which enter into the theory of scattering of light in crystals need to be taken into account also in the theory of X-ray diffraction. When a beam of common light traverses a crystal, its wavelength is very great in comparison with the spacing of the electronic stratifications in the crystal and the latter do not therefore reflect the incident radiation but merely transmit it. On the other hand, it is known that the passage of the light excites vibrations of the atomic nuclei with the result that if the incident light be monochromatic, scattered radiations are observed exhibiting sharply defined shifts of frequency corresponding to the characteristic vibration frequencies of the atomic nuclei about their positions of equilibrium. The appearance of such scattered radiations indicates the existence of a coupling between the forced vibrations of the electrons under the influence of the incident electro-magnetic field and the natural or free vibrations of the atomic nuclei about their positions of equilibrium. In the language of the quantum theory of dispersion, the appearance of such frequency shifts is described by the statement that the system composed of the nuclei and electrons does not—following the virtual transitions to higher energy states induced by the incident radiation—return to the same level as previously but shifts to a third level in which the atomic nuclei are in a different energy state of vibration.

In the X-ray experiment, the frequency of the incident radiation is usually much higher than the characteristic frequencies of the electrons. Nevertheless, the ideas of the quantum theory of dispersion continue to be applicable and the question therefore arises whether the incident X-radiations can also excite

transitions in the energy state of the atomic nuclei by virtue of their mechanical coupling with the electrons and if so, what would be the observable result of such transitions. We shall now proceed to answer these questions.

4. The characteristic vibrations of crystal lattices

As remarked earlier, the fundamental feature of crystal architecture is that it is a repetitive pattern in three-dimensional space of a characteristic unit of the structure containing a finite number of atoms. Each unit of the structure is similar to and similarly situated with respect to the units surrounding it. Hence it follows that in respect of all their physical properties the units of the crystal structure would be similar to each other; in particular the dynamic behaviour of all the units of the crystal structure would be completely identical. We may put the same situation in slightly different language by saying that every crystal is an assembly of atomic oscillators all of which have identical modes and frequencies of vibration. What these modes and frequencies are is a matter for rigorous mathematical investigation. Such investigations have been carried out and published in recent papers which have appeared in the *Proceedings* of the Indian Academy of Sciences. It emerges that all the atoms in the crystal have $(24p - 3)$ modes and frequencies of vibration in common. $(3p - 3)$ of these frequencies represent modes in which equivalent atoms in neighbouring cells oscillate with the same amplitudes and in identical phases, while for the remaining $21p$ frequencies, equivalent atoms in adjacent cells oscillate with the same amplitudes but with phases which may be the same or else opposite along one, two or all three axes of the lattice. This picture of the dynamical behaviour of the atoms in a crystal has important consequences for the subject of X-ray diffraction which we shall now proceed to consider.

5. A classical analogue

It is useful in the first instance to consider the position from a purely classical standpoint so that the consequences arising therefrom may be taken over into the quantum-mechanical treatment of the problem. We shall restrict ourselves here to a consideration of the $(3p - 3)$ modes of vibration of the atomic nuclei in which the vibrations in the different cells of the crystal lattice are identical in all respects. In such a vibration it would follow that the stratifications of electron density in the crystal would not remain in fixed positions but would oscillate to and fro with the frequency equal to that of the mode of vibration concerned. An X-ray beam traversing such stratifications would continue to be reflected in the same direction as in the static case. But in consequence of the periodic motion of the stratifications (assumed to be of small amplitude), the reflected X-ray beam would

now consist of three spectral components having frequencies respectively ν , $(\nu + \nu^*)$ and $(\nu - \nu^*)$, ν being the incident X-ray frequency and ν^* that of the oscillation of the lattice. The additional components arising by virtue of the oscillations may be regarded as Doppler shifts of frequency resulting from the movement of the stratifications normal to themselves. The amplitudes of the additional components would be determined by the ratio of the amplitude of the oscillations to the wavelength of the X-rays.

The above classical result translated into the language of quantum mechanics would mean that the incident X-radiation traversing the crystal may excite the characteristic vibrations of the lattice, and if such excitation actually occurs, the beam would be reflected in the same direction as in the absence of such excitation but with diminished frequency. If, on the other hand, the characteristic vibration is already present by reason of thermal agitation, the crystal may be de-excited and the incident X-radiation would then be reflected with increased frequency.

6. Infra-red activity and X-ray diffraction

It will be seen from the foregoing that the mechanism which can give rise to X-ray reflections of altered frequency is altogether different from the mechanism which results in the scattering of light with frequency shifts in crystals. In the latter case it is known that a change in the internuclear distances gives rise to a change in the optical polarisability of the elements of the structure and hence also to secondary radiations with altered frequency; the selection rules which determine whether a particular mode of vibration is or is not active in light-scattering are different from those which determine whether or not the same mode is active in infra-red absorption. In the X-ray problem, the shifts of frequency in the X-ray reflections arise from the periodic movements of the stratifications of the electron density associated with the nuclear oscillation. Hence, it may be expected that the excitation and the de-excitation of the lattice vibrations resulting from the passage of X-rays would appear in circumstances analogous to those in which infra-red absorption manifests itself. In other words, X-rays may be expected to excite or de-excite those oscillations of the lattice which are also infra-red active.

7. The geometry of the X-ray reflections

In the foregoing we have assumed that the vibrations in the crystal structure appear in all the cells of the crystal lattice not only with the same frequency but also with identical phases. This is evidently a highly idealised situation, which when it actually exists indicates that the X-ray reflection with altered frequency would appear in precisely the same direction as that of unmodified frequency. The modes and frequencies of the lattice vibrations are determined by the interatomic

forces which may be assumed to fall off rapidly in magnitude with increasing interatomic distances. Hence, a change of phase of the oscillations occurring progressively as we pass from cell to cell—provided it be small enough—would involve a relatively small change in the actual frequency of vibration. This would give rise to the possibility of observing X-ray reflections with a change of frequency even in settings of the crystal different from those in which the ordinary or unmodified reflections are observed. Such reflections may be regarded as arising from a forced oscillation of the lattice with slightly altered frequency and with the appropriate phases induced by the incidence of the X-radiation. In such circumstances the intensity of the X-ray reflection of altered frequency may be expected to fall off more or less rapidly as the setting of the crystal is altered from the setting needed for an ordinary reflection.

8. The influence of thermal agitation

As already indicated, it necessarily follows that if X-rays can excite an infra-red active oscillation of the lattice, they can de-excite such an oscillation if it already exists and thereby give rise to an X-ray reflection of increased frequency. The relative intensities of the X-ray reflections with increased and diminished frequencies respectively would be determined by the Boltzmann factor for the particular frequency of the oscillation of the lattice. The reflections of increased and of diminished frequencies would, of course, appear in the same direction, and it is the summation of their intensities that would determine the observed effects. Accordingly, measurements of the variations in intensity of this observable effect with temperature would enable us to estimate the frequency of the vibrations responsible for them.

9. Summary

The quantum theory of dispersion indicates that the infra-red active vibrations of the atoms in a crystal would be excited by the passage of a beam of X-rays through it. Such excitation would result in the incident beam being reflected by the lattice planes of the crystal with appropriately diminished frequency. Such reflections would also be observable but with diminished intensity when the setting of the crystal is moved away from the position in which X-rays of the given wavelength are selectively reflected by the lattice planes in question with unaltered frequency. The effect of thermal agitation is also considered.

New concepts of the solid state*

SIR C V RAMAN

My first duty is to thank the authorities of the Nagpur University on behalf of the Indian Academy of Sciences for the invitation which has enabled the Annual Meeting of the Academy to be held this year under the auspices of the University. The Fellows of the Academy deeply appreciate the labours of the Chairman and members of the local Committee and of Prof. Moghe in making the arrangements for the meeting and are grateful for the hospitality which has been generously provided for the occasion.

For good or for evil, we live in an age of science. No one who is familiar with the history of science would fail to recognize the great influence which has been exercised on its progress by the work of the various national academies of science, as for instance the Royal Society of London and the Academy of Sciences at Paris. The publications of these academies are the primary records of scientific discovery and invention in their respective countries. To no small extent, also, the Academies have been responsible for the promotion and encouragement of research work and for the co-ordination of the research activities of the Universities. During the seven years the Indian Academy of Sciences has been in existence, it has striven to fulfil these functions in our country. The *Proceedings* of the Academy which have appeared punctually, month after month, embody the best part of the research work done in most of the Indian Universities. It is greatly to be desired that these Universities appreciate what the Academy is doing for them and help the Academy to carry on under the present difficult conditions.

I propose to devote my address this year to an exposition of the new ideas concerning the solid state of matter which have emerged from recent investigations made at Bangalore. The vast majority of actual solids are crystalline in structure and are either single crystals or else consist of polycrystalline aggregates. The gateway to an understanding of the solid state is therefore to be found in the study of crystals. The most effective starting point for such a study is, again, the ultimate structure or atomic architecture of the solid. The physics of the solid state of matter indeed concerns itself largely with the relationship between

*Presidential Address to the Indian Academy of Sciences at the Annual Meeting held at the Nagpur University on the 24th of December 1941.

the atomic grouping in space which characterizes a crystal and the physical behaviour of the solid in various circumstances.

As is well known, crystals often possess beautiful external forms with specific geometric features. The symmetry characters of these geometric forms stand in the closest relation to the physical properties of the solid, such relationship being most evident when we consider those properties which vary with direction. The study of the geometric forms and of the physical properties of crystals resulted in the classification of crystal forms into six or seven systems and their further subdivision into thirty-two classes of crystal symmetry. It is natural that crystallographers were led by such studies also to speculate on the features in the internal architecture of crystals to which could be ascribed the external symmetry properties manifested by them. The theoretical investigations which dealt with this problem resulted in the recognition that a crystal is essentially a repetitive pattern in space and that the material particles of the solid are arranged in regular geometric order in a three-dimensional space-lattice. The discovery of the 14 possible kinds of space-lattice and of the 230 possible ways of grouping the atoms, each in its own appropriate type of space-lattice and coming under one or another of the 32 possible symmetry classes, gave the necessary precision and completeness to such general notions of crystal architecture.

The ideas of the mathematical crystallographers of the nineteenth century found a spectacular confirmation in Laue's great discovery made in 1912 of the diffraction of X-rays by the space-lattice of crystals. During the thirty years which have elapsed since that discovery, a vast amount of detailed knowledge regarding the structure of individual crystals has been built up by the labours of the X-ray crystallographers. Around such knowledge, again, there has been a great deal of discussion regarding the nature of the forces which held together the atoms, ions or molecules in a crystal in the form of a coherent solid.

It must be recognized that the concept of a regularly ordered assemblage of atoms, ions or molecules in a space-lattice is only a static description of crystal structure and does not suffice to give a complete view of the solid state. That the density and many other physical properties of a solid vary with temperature is clear indication that the atomic positions in a crystal are subject to disturbance by thermal agitation. A description of the possible atomic movements in a crystal is thus as important for crystal physics as a knowledge of the static structure. In other words, a dynamic picture of the crystalline state is required as a complement to the static picture furnished by the space-group theory. The possible modes of atomic vibration would evidently be determined by the atomic groupings in the crystal lattice and the forces that come into play when such grouping is disturbed. It follows that the static and dynamic aspects of crystal architecture should stand in the closest relationship to each other.

A dynamic concept of the solid state is necessarily the starting point in any consideration of the thermal properties of a crystal, e.g., its specific heat, thermal expansion or thermal conductivity. It is equally fundamental in any attempt to elucidate such physical properties of solids as are notably influenced by

temperature, e.g., the electrical resistivity of metals. The subject of crystal dynamics assumes a special importance in considering the effects arising from the propagation of electromagnetic waves through crystals, e.g., the scattering of light or the diffraction of X-rays. Spectroscopic and X-ray studies on crystals indeed afford us a penetrating insight into the problems of the solid state.

The theorists who have handled such problems in the past have proceeded by carrying over notions derived from the classical theory of vibrating elastic solids into the domain of atomic dynamics. The history of physics during the present century suggests that all such extrapolations from macroscopic to atomic concepts must be regarded with caution. The extrapolations made in the Debye and Born theories of crystal dynamics do not, however, appear to be justified even from a purely classical point of view. It is not surprising, therefore, that the conclusions derived from these theories fail to survive the test of comparison with the experimental facts in several different branches of research. Before we proceed to consider evidence of this kind, it appears desirable to examine the foundations on which these theories rest.

We may, in the first instance, comment on the well known specific heat theory of Debye which has had the run of the text-books of physics for many years and even yet seems to be in favour. The theory assumes that the thermal energy of a solid may be identified with the energy of elastic waves travelling within it, and gives an expression for the energy in terms of the velocities of these waves. That these assumptions are unjustifiable is evident from Debye's own formulae. For, the calculation shows that a very large proportion of the elastic vibrations must be assumed to possess wavelengths comparable with the lattice spacings of the crystal. Their frequencies also become comparable with those of the vibrations of the individual atoms. Even according to the classical principles, vibrations of such short wavelengths and high frequencies could scarcely be expected to travel through the crystal with the assumed acoustic velocities. Indeed, the familiar fact that thermal energy does not travel at all but only diffuses with extreme slowness in solids is a clear disproof of the basic assumptions of the Debye theory. Far from supporting the postulates of the theory, the facts point to exactly the opposite conclusion, namely that no sensible part of the thermal energy of solids consists of the elastic vibrations of macroscopic physics.

The so-called postulate of the "cyclic lattice" on which the crystal dynamics of Born is based was introduced by him as a mathematical device to escape the difficulties which he believed to arise from the unspecified conditions at the external boundary of the crystal. The postulate in effect prescribes "wavelengths" for the atomic vibrations in the crystal which bear no relation to its internal architecture but are related to its external dimensions in exactly the same way as the elastic vibrations of macroscopic physics. The postulate of the cyclic lattice has no theoretical justification and its introduction makes Born's approach to the problem of crystal dynamics wholly unreal and no less open to criticism than the theory of Debye.

The fallacy of the basic ideas underlying the Debye and Born theories becomes

evident when we consider the nature of the vibrations within a solid indicated by the classical theory of elasticity. The form and size of the external boundary of the solid determines the possible modes of elastic vibration. In each individual vibration, the motion at all points within the solid has a specifiable frequency and a coherent phase-relationship. But there would be an immense number of such modes with varying frequencies. The superposition of all such modes, assumed to be co-existent, would therefore result in the agitation within the solid being of a completely chaotic character, varying from point to point and from instant to instant without any recognizable periodicity in space or recurrence in time. Thus, in effect, the assumptions made in the Debye and Born theories are equivalent to the assertion that while the static arrangement of the atoms in a crystal is one of perfect order and regularity, the dynamic character of their movements is one of perfect chaos and disorder, indeed exactly of the same kind as the movements or vibrations of the molecules of a gas. This conclusion is obviously so improbable that we may well feel justified in rejecting without hesitation the premises on which it is based.

A crystal, as we have seen, is a periodic array of similar particles, similarly situated and capable of influencing each other's movements. It follows that the vibrations of such an assemblage should exhibit a high degree of orderliness, approaching the ideal of a perfectly, co-ordinated vibration in which the frequency, amplitude and phase are identically the same throughout the crystal. To picture such a vibration, we may first consider the group of the atoms present in an individual cell of the space-lattice. The internal vibrations of such a group would comprise several distinct modes determined by the number of atoms present. Each such vibration may then be pictured as occurring in identically the same way in every cell of the crystal lattice. Geometrically, such an oscillation could be represented as a periodic movement, relative to each other, of the interpenetrating simple lattices of similarly placed atoms of which any crystal may be regarded as built up. Such a vibration would have a uniquely definable frequency, and the vibration spectrum of the crystal would therefore consist of a finite number of discrete monochromatic frequencies.

Thus, instead of an infinite array of chaotic movements varying arbitrarily in phase from cell to cell of the crystal, and having a continuous spectrum of frequencies, we obtain a finite group of vibration modes with space-patterns coinciding with the lattice structure of the crystal and having a set of discrete monochromatic frequencies. These vibrations are essentially periodic changes in the fine structure of the crystal and do not involve mass movements of the substance of the solid. Hence, neither the existence of an external boundary nor the conditions restraining its movements can have any influence on such vibrations.

The most appropriate choice for the space unit of the three-dimensional repetition-pattern of the atomic vibrations is evidently that which enables all the modes possible to be included without redundancy. Hence the appropriate choice

is not the cell having the smallest dimensions or including the least number of atoms, but one which is fully representative of the crystal structure and symmetry. In the majority of crystals, the number of atoms included in such a space-unit would be fairly large. Hence, the internal vibrations of the group of atoms contained in it would comprise the largest proportion of the available degrees of freedom of movement, indeed all except a small residue representing the translatory movements of the chosen cell. To enable these latter to be included in the scheme, we may consider the internal vibrations of a group of atoms contained in the cells of a super-lattice having cells of twice the linear dimensions and therefore of eight-fold volume. Proceeding in this way by successive steps, the vibration spectrum of the crystal could be developed with all desirable completeness as a set of monochromatic frequencies.

It will be realised that the geometric characters as well as the frequency distribution of the atomic movements in crystals obtained in this way would be radically different from those indicated by the Debye and Born theories. It is evident also that the new concepts involve striking differences in the spectroscopic, X-ray and thermal behaviour of crystals as compared with those derived from the older ideas. The issues arising between the new and the older concepts are thus capable of being brought to an exact experimental test.

The atomic vibrations in crystal lattices are accessible to optical and spectroscopic investigation in several different ways. A method which makes the entire frequency range conveniently accessible to observation is the spectroscopic study of the scattered radiations emerging from a crystal traversed by monochromatic light. The most striking feature revealed by such studies with crystals is the extreme sharpness of the displaced lines appearing in their spectra. Even in those cases where the lines are somewhat diffuse, they sharpen into the finest lines when the crystal is cooled down to low temperatures. The monochromatism of the lattice frequencies thus indicated is especially significant when the vibrations are observable only in the crystalline state, in other words when the lines disappear in the molten or dissolved material. These facts are wholly inconsistent with the Debye and Born theories. Indeed, it may be said that the character of the spectra observed even with the simplest of crystals bears no resemblance to the diffuse continua suggested by these theories. Evidence confirmatory of the new concepts of crystal dynamics is also furnished by the absorption and luminescence spectra of crystals observed at low temperatures, e.g., diamond. Here again, the lattice spectrum is revealed as a set of discrete monochromatic frequencies stretching down to low values, in startling contrast with the conclusions of the Debye and the Born theories.

As already explained, the new concepts indicate a close correspondence between the static structure and the dynamic behaviour of a crystal, in other words that the atomic vibration patterns are either identical with or closely related to the lattice structure of the crystal. As an immediate consequence of this relationship, it follows that the lattice planes of a crystal should give two distinct

types of X-ray reflection—a dynamic reflection with altered frequency in addition to the static reflection of unmodified frequency discovered by Laue. The more perfectly co-ordinated is the oscillation of the lattice structure, the more perfect would be the geometric character of the dynamic X-ray reflections. Hence, these reflections should be shown in the most striking way by diamond-like structures in which the entire crystal is practically a single molecule and less perfectly by other crystals in which the lattice structure is of a more open kind.

That the lattice planes in crystals do give the new type of dynamic X-ray reflection here indicated and that such reflections are incapable of being explained on the older theories was discovered and announced by myself and Dr Nilakantan in March 1940. In a symposium of fifteen papers published in the *Proceedings* of the Academy for October 1941, the theory of these new X-ray reflections, their relation to quantum mechanics and the experimental facts as observed with diamond and numerous other crystals have been thoroughly explored. It has been proved that the experimental facts are, on one hand, fatal to the Debye and Born theories and that on the other hand, they give the strongest support to the new concepts of the solid state.

To the pioneer investigations of Einstein, we owe the basic principles of the quantum theory of the specific heat of solids. He showed clearly that the thermal energy of a crystal stands in the closest relation to its optical properties and could, in fact, be expressed in terms of the characteristic frequencies of atomic vibration appearing in the infra-red region of frequency. In his earliest paper, Einstein suggested that the atomic frequencies could be assumed to be monochromatic. Considering one such characteristic frequency in the case of diamond, he evaluated the same from the specific heat data. It will be seen from our present discussion that the basic assumption of monochromatism was justified, and that the only amendment needed in Einstein's theory was the inclusion of the full number of discrete monochromatic frequencies demanded by the lattice structure of the crystal with the appropriate statistical weights. It is also seen that the application of the macroscopic theory of elastic vibrations due to Debye, successful though it seemed at the time, was, in reality, a false step.

In a symposium of seven papers published in the *Proceedings* of the Academy for November 1941, the problem of the thermal energy of crystalline solids has been discussed fully from the new point of view and compared with the experimental data for a variety of substances. In several cases where the necessary spectroscopic data were available, these have been effectively made use of. In other cases, e.g., metals, the specific data themselves have been utilised to evaluate the atomic frequencies. The most significant fact which emerges from the symposium is that the experimental facts in several cases which refused obstinately to fit into the Debye and Born theories find a natural explanation in the new concepts without the aid of any special hypothesis.

Summary

The postulates on which the Debye theory of the specific heat of solids and the Born crystal dynamics are respectively based have been critically examined and shown to be theoretically untenable. Since a crystal is a three-dimensionally periodic grouping of similar oscillators coupled together, it follows that the modes of vibrations possible would be also space-periodic, the geometric modes being determined by the characters of the atomic space-grouping in the crystal. They would further form a finite and enumerable set of monochromatic frequencies. The spectroscopic, X-ray and thermal behaviours of a crystal would on these views be radically different from those consequent on the Debye and Born theories. The experimental facts are found to contradict the conclusions of these theories and on the other hand, to be in full accord with the new concepts.

The vibration spectrum of a crystal lattice

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1. Introduction

It is a fundamental problem in the physics of the solid state to determine the possible modes and frequencies of vibration of the atomic nuclei in a crystal about their positions of equilibrium. The importance of the problem will be evident when we recollect that there is scarcely any physical property of a solid which is not influenced in greater or less measure by the thermal agitation of the atoms, and that the existence of atomic vibrations (excited thermally or otherwise) comes into evidence in a variety of phenomena exhibited by crystals. We may, in particular, mention various optical effects observed with crystals, e.g., the scattering of light with altered frequency, luminescence and absorption spectra at low temperatures, which not only render the existence of atomic vibrations in them obvious, but also enable us to make precise determinations of their vibration frequencies, and even infer their geometric characters.

An appropriate starting point for the inquiry is furnished by the well known result in analytical mechanics that all the possible small vibrations of a conservative dynamical system about a position of stable equilibrium may be represented as a superposition of certain modes of vibration designated as the normal modes of the system. In each such mode, the particles of the system execute harmonic vibrations with a common frequency characteristic of the mode, and all pass simultaneously through their positions of equilibrium at some particular phase of the vibration. The question arises for investigation, does the structure of a crystal possess any normal modes of vibration as thus defined, and if so, what are their frequencies? In seeking an answer to this question, it is obviously not permissible to make in advance any arbitrary postulate regarding the nature of the normal vibrations, since this is itself the subject-matter of the investigation. Further, it is essential that we assume the most general type of interaction possible between the atoms in the crystal which is consistent with its known structure and symmetry properties. Indeed, in an investigation intended to deduce results of general application, it is evidently undesirable to make any special postulates regarding the interatomic forces, viz., that they are only

operative as between contiguous atoms or that they are in the nature of central forces whose magnitude varies as some power of the distance. The introduction of arbitrary postulates and assumptions has indeed, as will be shown in this paper, led to misleading results in the past history of the subject.

2. The Lagrangian equations of motion

We denote the displacements of a chosen atom in a particular cell of the crystal structure from its position of equilibrium by the symbols q_{xrs} , q_{yrs} , q_{zrs} , these being parallel respectively to the three mutually perpendicular co-ordinate-axes x , y and z . Here r is an index number indicating a particular atom amongst the p atoms in the cell of the crystal structure, while s is an index number indicating the particular cell in which the atom is located. The symbols $q_{x\rho\sigma}$, $q_{y\rho\sigma}$, $q_{z\rho\sigma}$ have similar significance, except that ρ and σ which are the atom and cell indices respectively are regarded as unspecified. The masses of the atoms are written as m_r or m_p .

The kinetic energy T of the vibrations of the crystal is accordingly given by the summation over all possible values of ρ and σ of the expression

$$\frac{1}{2}m_p[\dot{q}_{x\rho\sigma}^2 + \dot{q}_{y\rho\sigma}^2 + \dot{q}_{z\rho\sigma}^2]. \quad (1)$$

The potential energy V of the displacements of the atoms from their positions of equilibrium is given by the summation of all the terms derived from the expression

$$\frac{1}{2}K_{xrs}^{y\rho\sigma} \cdot q_{xrs} \cdot q_{y\rho\sigma} \quad (2)$$

by making r , s , ρ , σ run over all the possible values, as also by interchanging x , y and z . The dependence of the force-constants jointly on x , r , s and y , ρ , σ is indicated by the indices attached to them. It is evident that

$$K_{xrs}^{y\rho\sigma} = K_{y\rho\sigma}^{xrs}. \quad (3)$$

Hence, since each distinct pair of co-ordinates appears twice over in the summation, we may replace the factor $\frac{1}{2}$ by 1 in (2), it being understood that they are written together only once. The factor $\frac{1}{2}$ is however retained for the terms which appear as the squares of the displacements.

The equation of motion which must be satisfied by any particular co-ordinate, e.g., q_{xrs} is

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_{xrs}} \right) + \left(\frac{\partial V}{\partial q_{xrs}} \right) = 0. \quad (4)$$

If we assume that the vibration under consideration is a normal mode for the crystal, the displacement-components of all the atoms must be of the form $q \sin \omega t$ where the q 's are real quantities depending on the atom chosen and the direction

of its displacement, while ω is the same for all atoms in the crystal. On this basis the equation for q_{xrs} becomes

$$(m_r\omega^2 - K_{xrs}^{xrs})q_{xrs} = \sum_{y\rho\sigma} K_{xrs}^{y\rho\sigma} \cdot q_{y\rho\sigma}. \quad (5)$$

The summation indicated on the right-hand side of (5) is to be understood as including the contributions due to all the displacement-components of all the atoms in the crystal with the single exception of the displacement q_{xrs} under consideration which appears on the left-hand side of the equation. There would, of course, be a whole series of equations of this type for the x , y and z displacements of every atom in the crystal, and it is necessary that all these equations are simultaneously satisfied for the given value of ω , for the vibration under consideration to possess the characters of a normal mode.

3. The solution of the equations

The clue to the discovery of the normal modes of vibration is furnished by the basic principle of crystal architecture which may be stated as follows: *A crystal consists of sets of equivalent atoms ordered in such manner that each atom in a set is both geometrically and physically related to its environment in exactly the same way as every other atom of the same set.* From this it follows that the force-constant which connects the displacements of any pair of atoms in the crystal is the same as that which connects the displacements of any other pair of atoms, provided that the two pairs of atoms can be simultaneously brought into coincidence by simple translations of the crystal lattice parallel to its axes.

Consider now the equation of motion analogous to (5) for the r th atom in a different cell, say s' . In writing it down, it is convenient to choose a running cell-index σ' different from the σ appearing in (5), but so related to it that the translations of the crystal lattice which would bring s' into coincidence with s would also bring σ' into coincidence with σ . We have then

$$(m_r\omega^2 - K_{xrs'}^{xrs'})q_{xrs'} = \sum_{y\rho\sigma'} K_{xrs'}^{y\rho\sigma'} \cdot q_{y\rho\sigma'}. \quad (6)$$

Now the relation between s , σ and s' , σ' assumed above, taken in conjunction with the physical structure of the crystal, gives us at once the relations

$$K_{xrs}^{xrs} = K_{xrs'}^{xrs'}, \quad (7)$$

$$K_{xrs}^{y\rho\sigma} = K_{xrs'}^{y\rho\sigma'}, \quad (8)$$

between the force-constants appearing in (5) and (6). This identity of the force-constants appearing on both sides of the equations of motion of equivalent atoms suggests that their displacements in a normal mode of vibration are also related to each other in a simple way. Algebraically, it is evident that if there exists

between them a general relationship of the form

$$\frac{q_{xrs}}{q_{xrs'}} = \frac{q_{y\rho\sigma}}{q_{y\rho\sigma'}}, \quad (9)$$

it follows therefrom that when equation (5) is satisfied, equation (6) will also simultaneously be satisfied, and indeed also the similar equations for *all* the equivalent atoms of index r in the crystal. Further, if the general relations indicated in (9) subsist, they are sufficient to ensure that when the equations of motion of an atom of *any* chosen index number in a particular cell are satisfied, the equations of all the other equivalent atoms of the same index number in every other cell of the crystal lattice are also simultaneously satisfied; the latter is a necessary condition for the vibration to be a normal mode.

4. Nature of the normal modes

We shall now consider more closely the significance of the relations stated in (9). They may be written in the form

$$\frac{q_{y\rho\sigma}}{q_{xrs}} = \frac{q_{y\rho\sigma'}}{q_{xrs'}}. \quad (10)$$

Stated in words, the meaning of (10) is that the vibrations of the equivalent atoms in the crystal are quantitatively related to the vibrations of the other atoms forming their respective environments in an identical fashion. *Prima facie*, this is what we should expect, since equivalence of geometric position in the crystalline array of atoms necessarily involves an equivalence in the strength of the forces holding the atoms together as indicated in equations (7) and (8), and hence should result also in equivalence in respect of dynamic behaviour in a normal vibration. To make the meaning of such equivalence clearer, we may return to equation (9) and take a case in which the cells s and s' occupy contiguous positions along one of the axes of the Bravais lattice. It follows that σ and σ' would similarly occupy contiguous positions along a parallel axis. Equation (9) thus signifies that the ratio of the corresponding displacements of *any pair* of contiguous equivalent atoms in the crystal lattice is a constant characteristic of the particular axis and of the particular normal mode under consideration.

We may apply the same arguments to cells contiguous to each other respectively along the second and third axes of the Bravais lattice. The three characteristic constants thus obtained need not necessarily be the same, and we therefore denote them by α , β , γ respectively. Since the atomic displacements are real quantities and their phases in a normal mode are all either the same or opposite, the constant ratios α , β , γ must be assumed to be *real* quantities which may be either positive or negative. If, starting from a particular cell, we move out

to another which is reached by u , v , w primitive translations in the positive directions along the three axes of the Bravais lattice, the amplitude of the vibration of corresponding atoms would be altered in the ratio $\alpha^u \beta^v \gamma^w$, while if we similarly proceed in the negative direction, we would reach a cell in which the amplitudes are altered in the ratio $\alpha^{-u} \beta^{-v} \gamma^{-w}$. Hence, if α or β or γ is numerically different from unity, we may, by proceeding sufficiently far in one direction or another from an arbitrarily chosen cell where the amplitude is small, reach cells where the amplitudes are larger than any assigned limit. Hence, the initial postulate that the vibration amplitudes are everywhere small can only be sustained if the constants α , β , γ are numerically equal to unity, and are either positive or negative. We thus obtain the result

$$\alpha = \pm 1, \quad \beta = \pm 1, \quad \gamma = \pm 1. \quad (11)$$

The possible choices from amongst the alternative signs in the three equations (11) are evidently independent. We have therefore *eight* possible cases, all of which are covered by the following description: *Equivalent atoms in the crystal have all the same amplitude of vibration, their phases being either the same or else opposite in successive cells of the lattice along each of its three axes.* We may also describe the position as follows: *The atomic vibrations repeat themselves exactly in a space-pattern of which the unit has twice the dimensions in each direction and therefore eight times the volume of a unit cell of the crystal lattice.* We may interpret these statements physically by considering the well known result of coupling two exactly similar oscillators to each other, namely the appearance of two types of vibration in which the oscillators have the same phase and the opposite phases respectively. In other words, the dynamic behaviour of a crystal is a three-dimensional analogue of the case of two coupled oscillators.

5. Enumeration and description of the modes

We have now to consider the question whether the relations stated above in equation (11) uniquely determine all the possible normal modes of the atomic vibrations in a crystal. The readiest way in which we can satisfy ourselves that this is the case is by considering the question from a physical point of view. The significance of equation (11) can be stated in the following manner: *In every normal mode of vibration, the energy of the vibration is the same for every individual cell of the crystal lattice, while the amplitudes have either the same signs or else have alternately opposite signs in the successive cells.* The two parts of the proposition are complementary and taken together characterise the normal modes completely. It is easy to see that no vibration in which either or both of these characters is departed from can be a normal mode. If, for example, the energy of the vibration were to vary from cell to cell, it would be obviously not possible for

such a state of affairs to continue permanently in a homogeneous structure. Energy would be progressively transferred from the cells having the greater energy to those having less, and the nearer the cells are to each other, the more rapidly would this process occur. A normal vibration is, by definition, perfectly time-periodic and hence, the equality of the energy of vibrations in the different cells is a necessary feature of it, and this in turn is only possible if equivalent atoms have the same amplitude of vibration. It only remains therefore to consider the question of the phases. Here, again, the definition of a normal mode allows only two alternatives, namely a positive or a negative amplitude. The effect of reversing the phase of the vibration of the atom without altering its amplitude is to change the sign of the term contributed by it to the equation of motion of every atom in the crystal, leaving its magnitude unaltered. From this, it follows that equations (5) and (6) cannot be simultaneously satisfied unless all the corresponding atomic displacements have the same signs in the two equations or alternatively have all the opposite signs. These requirements are satisfied by the eight dispositions indicated by equations (11), but not by any other conceivable arrangement of positive and negative amplitudes of equal magnitude over the cells of the lattice.

The relations stated in (11) enable us to reduce the number of independent equations of the type (5) which have to be solved from an infinite set to just $3p$ equations for each of the eight distinct cases arising therefrom. The constants appearing on the left-hand side are, of course, different in each of the $3p$ equations of each set. The terms appearing on the right-hand side of each equation may be grouped into sets in which each of the $(3p - 1)$ co-ordinates involved appears multiplied by what is technically an infinite series. Physical considerations, however, indicate that these series should be convergent and summable. Each of them may therefore be replaced by a single new constant. In other words, for each of the eight distinct cases arising from (8), we may frame a set of $3p$ equations connection the $3p$ co-ordinates, the constants appearing in them having new values. The solution of the sets of equations thus obtained would enable both the normal modes (viz., the ratios of the atomic displacements) and the normal frequencies to be evaluated.

It thus becomes evident that the number of normal modes and normal frequencies for each of the eight cases arising from (8) is $3p$. In other words, we have $24p$ normal modes and normal frequencies, which is the same number as the degrees of freedom of the $8p$ atoms whose vibrations form the repeating pattern in space. It should, however, be remembered that we have started from the assumption that the crystal as a whole is at rest. Its centre of gravity must therefore remain fixed, and this gives three conditions of constraint which would reduce the number of solutions by 3. Thus in all, we have only $(24p - 3)$ normal modes and frequencies of vibration. The individual cell of the crystal lattice is the unit of the repeating pattern in space for $(3p - 3)$ of these modes, the atoms in the cell vibrating against each other. The repeating pattern in space for the remaining

$21p$ normal modes is the super-cell already considered which has twice the dimensions and eight times the volume of a unit cell of the lattice.

It is possible to give simple geometric descriptions of the eight different types of normal modes arising from equation (11). The modes described by $\alpha = 1, \beta = 1, \gamma = 1$ may be pictured as oscillations with respect of each other of the p interpenetrating Bravais lattices of atoms of which the crystal is built up. There would be $(3p - 3)$ such modes, while the other 3 degrees of freedom of these lattices may be identified as simple translations of the entire crystal which we have already excluded from the scheme. The remaining $21p$ normal modes may be pictured as oscillations relative to each other of the alternate planes of equivalent atoms in the crystal. If for example, $\alpha = 1, \beta = 1$ and $\gamma = -1$, the alternate planes of the atoms containing the α and β axes and intersecting the γ axis would oscillate against each other. If $\alpha = 1, \beta = -1, \gamma = -1$, the alternate planes of atoms passing through the α axis and cutting both the β and γ axes would oscillate against each other. If α, β, γ are all negative, the oscillating planes of atoms would intersect all the three axes at the appropriate angles. In the case of a cubic crystal, for example, the oscillating planes of atoms would be those respectively parallel to the cubic, dodecahedral and octahedral faces of the crystal.

6. Nature of the atomic frequency spectrum

The result which emerges from the foregoing discussion is that the *vibration spectrum of the crystal consists of a set of discrete monochromatic frequencies which may be described as arising from the vibrations against each other of the atoms located in the units of an 8-cell super-lattice*. In deducing this result, we have regarded the crystal as a three-dimensionally periodic structure infinitely extended in space, and ignored the existence of any external boundary. This procedure appears justified. For, in the equations of motion of an atom, the terms contributed by the other atoms in the crystal must necessarily be assumed to form a convergent series, in other words, their influence on its motion reaches a limiting value when the size of the crystal is increased indefinitely. Hence, the presence or absence of an external boundary can make no sensible difference to the modes of the atomic vibrations in the interior of the crystal.

It may be remarked also that the number of discrete frequencies observable would be very considerably diminished if the crystal belongs to a class exhibiting a high type of symmetry. For, in such a case, several of the modes of vibration reckoned as distinct in the preceding enumeration would possess identical frequencies. Taking for instance a crystal of the cubic system, we recognize that the symmetry of the crystal would result in the eight distinct sets of frequencies indicated by equation (8) being in effect reduced to four. In one set of normal modes, all equivalent atoms in the crystal move in the same phase: in three sets of normal modes, the equivalent atoms so moving lie in planes parallel to one or

another of the cube faces and the corresponding frequencies would therefore be the same; in three others again, planes of atoms parallel to the dodecahedral faces move in the same phase, and the corresponding frequencies will therefore be identical: in the eighth set, the planes of atoms moving in the same phase are parallel to the octahedral faces. The total number of distinct frequencies possible is thus reduced from $(24p - 3)$ to $(12p - 3)$. A further reduction will arise if the directions of movement of the atoms in normal modes reckoned as distinct in this enumeration are actually equivalent. For instance, the existence of a normal mode in which all the equivalent atoms oscillate parallel to one of the cube axes necessarily involves the possibility of two others having the same frequency. In these and other ways, a very considerable reduction in the number of distinct frequencies and consequent simplification of the vibration spectrum would result.

7. Elastic vibrations of the crystal lattice

As already remarked, the $24p$ degrees of freedom of the atoms contained in the cells of the super-lattice gives us only $(24p - 3)$ normal modes of atomic vibration. The 3 degrees of freedom of translation of the super-cell left over in this enumeration must therefore be assigned to modes of vibration of a different nature. The natural assumption to make is that they represent the lower frequencies of vibration coming under the general description of elastic vibrations of the crystal lattice. On this basis, the elastic vibrations represent only one-eighth of the total number of degrees of freedom in the case of crystals consisting of a single Bravais lattice, one-sixteenth of the number when there are two interpenetrating Bravais lattices, and a still smaller proportion when there are three, four or more atoms in the unit cell, finally becoming a negligible fraction of the whole in crystals of even moderately complex structure.

According to the classical theory of elasticity, waves of any frequency and of corresponding wavelength are possible within an infinitely extended solid, but specific modes of elastic vibration can only exist in a solid of finite extension, its shape and dimensions determining the modes as well as their frequencies. As we have seen, however, an atomistic approach gives a wholly different result, viz., that the normal modes and frequencies are determined by the internal structure of the crystal, the form and dimensions of the external boundary being irrelevant. The apparent contradiction between these conclusions disappears when we notice that the classical theory of elasticity describes the low-frequency region of the vibration spectrum, while the atomistic theory describes the high-frequency end. The two types of vibration differ in important respects. In the atomic vibrations properly so called, the absolute and relative atomic displacements are throughout of comparable magnitude, while in the elastic vibrations, the translatory movements of the lattice cells are greater than the relative atomic displacements approximately in the ratio of the wavelength to the cell dimen-

sions. While the two types of vibration may possibly tend to resemble each other in a transitional range, we are not justified in extrapolating either theory into the region of frequency in which it is wholly inapplicable.

The inappropriateness of the elastic solid theory in considering the high-frequency vibrations of a crystal lattice needs to be particularly emphasised. The theory is based on the idea that the material is a continuum having a uniform density and elasticity, whereas in reality, the crystal has a discrete atomistic structure. X-ray investigations show that the electron-density in a crystal is not uniform but is a triply-periodic function of position. The Fourier components of the electron density have noteworthy amplitudes, but they fall off with increasing order rapidly. The discontinuity of crystal structure is even more striking when we consider the mass-distribution. This is concentrated at the individual lattice points occupied by the atomic nuclei, and a Fourier analysis of the density distribution would therefore give component amplitudes which do not diminish with the order and each of which would by itself be greater than the average density of the crystal (by a factor of two in the case of a single set of atomic planes). This is a state of affairs very remote indeed from the uniform mass-density and elasticity assumed in the classical theory. Hence, only when the elastic wavelengths are large compared with the crystal spacings could we expect a concordance between the facts and the results of that theory. For smaller wavelengths and higher frequencies, the theory must fail, as is evident when we consider the behaviour of elastic waves in a medium exhibiting very pronounced stratifications of mass density or elasticity. If the Fourier components of space-variation of density were *small*, we would have selective reflections of the elastic waves analogous to the familiar optical or X-ray reflections by stratified media. The *large* amplitude of the Fourier components of mass-density however alters the situation radically, and it is readily shown that *the bands of selective reflection of the elastic waves would broaden so greatly as to result in a complete cut-off of the high-frequency region of the spectrum.** In the region of high frequencies, therefore, the ideas of the elastic solid theory are wholly irrelevant and inapplicable, and an atomistic approach to the theory becomes absolutely necessary.

One might, on the other hand, be tempted to carry over the atomistic approach which proves successful in the high-frequency region towards lower frequencies. To do this, one may assume that modes of vibration exist in which groups of atoms, as for example the super-cells considered earlier in the paper, oscillate within the crystal against other super-cells of the same kind, forming a repetition pattern of vibrations in which the space-unit is a giant cell having four times the dimensions and sixty-four times the volume of the unit cell of the crystal lattice. *Pro forma* equations of motion may even be framed for the oscillation of such

*Cf. Scientific Papers of the late Lord Rayleigh, Vol. III, Art. 142, Equation (74); *Philos Mag.* 24 145 (1887).

groups and the possible solutions discussed on the same lines for the atomic vibration, giving us eight sets of possibilities of the same kind as those given by (11); one of these, namely that in which all the super-cells vibrate in the same way should be excluded, as this would involve displacements of the centre of inertia of the entire crystal. The 8×3 or 24 degrees of freedom of oscillation of the super-cells contained in the giant cell would thus give us 21 modes of vibration, leaving as before, 3 degrees of freedom to be assigned to still lower frequencies of vibration. In the case of crystals of high symmetry, the number of distinct frequencies thus arising would naturally be reduced much below the maximum of 21.

An approach of the kind suggested above is obviously lacking in rigour, since it leaves the movements of the individual atoms within the oscillating super-cells unspecified. It is however not without value, since it indicates that as we come down the scale of frequency, the vibrations in the lattice may tend to take on the character of group movements which are intermediate in character between the purely atomic vibrations occurring at the high-frequency and the purely mass movements at the low-frequency end. The configuration of the vibrating groups bears a specific relation to the structure of the crystal instead of, as in the elastic vibrations, being determined solely by the form and dimensions of the external boundary of the crystal. It is also clear that the frequencies of the group movements would be related to the size of the groups in much the same way as the frequency of elastic waves is related to their wavelengths. If such group oscillations exist, as seems not unlikely in the higher ranges of the elastic spectrum, the frequency distribution in the latter would tend to approach the discreteness characteristic of the atomic vibration spectrum, instead of being continuous as indicated by the classical theory of elasticity.

8. Remarks on some earlier theories

The close analogy between the vibration-spectra of molecules and of crystals indicated by the foregoing theory receives unmistakable support from the results of the experimental investigation of crystal spectra by the several distinct methods to which reference has been made earlier in the paper. The results of the present theory are however in striking contrast with the ideas widely prevalent at the present time regarding the nature of the atomic vibrations in crystals. It is necessary, therefore, at this stage to make some critical comments on the earlier views which have found currency in the literature of the subject.

The well known and closely allied theories of Debye and Born on the atomic vibrations in solids were put forward about the same time (1912) in order to explain their thermal behaviour at low temperatures. As was shown earlier by Einstein in 1907, however, the frequencies of the atomic vibrations which constitute the thermal energy of a solid lie in the infra-red region of the

electromagnetic spectrum. It follows that the evaluation of the specific heat of a solid must depend on a knowledge of its spectroscopic properties in the infra-red frequency region. The experimental spectroscopic data for solids available in 1912 were, however, of a very meagre description. This may have been the reason why Debye and Born sought a different path from that indicated by Einstein and endeavoured to calculate the specific heat of solids by identifying their thermal energy with the energy of elastic vibrations of all possible frequencies. However, recent spectroscopic studies with many crystals, including especially several of the simplest chemical composition, show this identification to be unjustifiable. For, *they reveal numerous characteristic or monochromatic frequencies lying in the remotest infra-red*, in other words, within just the region which was sought to be described as a continuous spectrum of elastic vibration frequencies.

Both Debye and Born assumed that the normal modes of atomic vibrations have the same relation to the external dimensions of the solid as do the vibrations of the elastic type. This assumption is not, however, a reasonable one, since the modes and frequencies of the *mass* movements involved in elastic vibration and the modes and frequencies of *atomic* vibration depend on wholly different factors. These are the macroscopic properties and dimensions of the solid for the former, while for the latter they are the individual masses of the atoms and the manner in which they are arranged and bound together in the fine structure of the crystal. The considerations already set out above indicate that the external boundary of the solid can have no determining influence either on the normal modes or the normal frequencies of the atomic vibrations. On the other hand, the size and shape of the solid is the principal factor in determining the normal modes and frequencies of its elastic vibrations.

It is thus evident that theoretical considerations and experimental facts alike compel us to reject the assumptions on which the Debye and the Born theories are based.

9. Born's postulate of the cyclic lattice

In the Born theory, the lattice structure of the crystal is formally taken into consideration on the basis of the so-called "Postulate of the Cyclic Lattice".* This postulate assumes the *phase* of the vibration to alter progressively along each of the axes of the Bravais lattice in such manner that the "phase-wavelength" is a sub-multiple of an arbitrary chosen length which is itself a large integral multiple of the lattice spacing. Thus, for each axis, the number of possible phase-wavelengths is equal to the number of lattice spacings contained in the given length, and when all the three axes are considered, the total number of

* *Problems of atomic dynamics*, by Max Born, 1926, p. 193.

possibilities becomes equal to the total number N of lattice cells contained in the assumed large volume of the crystal. When multiplied by $3p$ (the number of degrees of freedom of motion of the atoms in each cell), the total number of possibilities is increased to $3Np$. Each of these is assumed to represent a possible normal mode of vibration with a corresponding frequency. Since the lengths of the "phase-waves" are assumed to be the various sub-multiples of an arbitrarily assumed large multiple of the lattice spacing, they bear no simple relation to the crystal spacings themselves. Indeed, the phase-wavelengths postulated crowd up increasingly as they become smaller, and hence the vast majority of them have values *intermediate* between small integral multiples of the lattice spacing. It is not surprising therefore that the Born theory yields an immense array of frequencies which form a diffuse continuous spectrum and which correspond to the assumed practically infinite array of possible phase-wavelengths.

From the statement made above regarding the Born postulate[†], it will be evident that it is equivalent to taking the ratios α , β , γ considered in section 4 of the present paper as imaginary quantities, viz.,

$$\alpha = e^{i\phi}, \quad \beta = e^{i\psi}, \quad \gamma = e^{i\chi}. \quad (12)$$

As already pointed out however, such an assumption would be illegitimate, since in any normal mode the phase of vibration must everywhere be either the same or the opposite, in other words, the only possible values of ϕ , ψ , χ are either 0 or π , making α , β , γ equal to either plus or minus unity, as indicated in our equation (11). If, on the other hand, it be suggested that equation (12) does not refer to a normal vibration but only to a "wave" in the lattice, then before it could be used for calculating the possible frequencies of atomic vibration, it would be necessary to show that the real amplitudes obtained by superposing on it another "wave" in the opposite sense given by

$$\alpha = e^{-i\phi}, \quad \beta = e^{-i\psi}, \quad \gamma = e^{-i\chi}, \quad (13)$$

would satisfy the requirements for a normal vibration. The result of superposing the "waves" represented by (12) and (13) would be to give a vibration of which the amplitude is proportional to the product $\cos(\phi l_1) \cos(\psi l_2) \cos(\chi l_3)$ where l_1, l_2, l_3 are the three cell index-numbers counted respectively along the three axes. As already remarked, however, Born's phase-wavelengths bear no simple relation to the crystal spacings, and hence the product $\cos(\phi l_1) \cos(\psi l_2) \cos(\chi l_3)$ and therefore also the energy of vibration would vary from cell to cell within the crystal. This is a state of affairs which cannot possibly exist in a normal vibration, and it follows that except when ϕ , ψ and χ are each chosen equal to 0 or π , the

[†]*Handbuch Der Physik, Zweite Auflage*, Article by Max Born and M Goppert-Mayer, 1933, 24/2 p. 642.

Born phase-waves do not correspond to any real or possible normal modes of vibration. Thus, it is evident that the whole immense arrays of atomic frequencies given by the Born theory are “manufactured” by his assumption of modes of vibration which are physically impossible and that they do not possess any physical meaning or significance.

The Born postulate is in the clearest contradiction with the experimental facts observed in crystals. As an illustration, we may choose the case of diamond in view of the simplicity of its structure. The unit cell of the diamond lattice contains two atoms, and the Born theory would therefore yield a continuous spectrum with two optical and two acoustic branches, and hence exhibiting (at the most) four diffuse peaks or maxima. On the other hand, according to the present theory, the atomic vibrations in the 8-cell super-lattice would have $(2 \times 24 - 3)$ or 45 modes, but on account of the high symmetry of the crystal, the number of distinct frequencies would be reduced to 8. The highest of these frequencies represents the oscillation of the two interpenetrating lattices in the crystal against each other and appears as a sharp and intense line with a frequency-shift 1332 cm^{-1} in the spectrum of the scattering of light by diamond. The remaining seven modes of lower frequency are longitudinal or transverse oscillations against each other of the planes of equivalent atoms in the crystal lying parallel to the faces of the cube and the octahedron. Several distinct methods of investigation of the lattice spectrum of diamond are available, the results of which are an independent check on each other. The spectroscopic studies of P G N Nayar* show the existence of a whole series of discrete frequencies from 1332 cm^{-1} downwards, and the values for these frequencies as deduced from the scattering, fluorescence and absorption spectra are in complete agreement with each other. While Nayar's experimental results find a natural explanation on the theory set forth in the present paper, they are wholly irreconcilable with the Born postulate and its consequences.

10. Summary

Starting from the most general expression for the potential energy of the displacements of the atoms in a crystal from their positions of equilibrium, their normal modes of vibration are derived. It is shown that in all the possible modes, the equivalent atoms in the crystal have all the same amplitude of vibration and either the same phase or alternately opposite phases in the successive cells of the lattice along each of its three edges. The vibrations thus form a repeating pattern in space of which the unit has twice the dimensions and eight times the volume of the lattice cell. The vibration modes are closely analogous to that of a molecule

*P G N Nayar, *Proc. Indian Acad. Sci.* **15** 293 (1942).

with the appropriate symmetries and containing eight times the number of atoms included in the lattice cell. The spectrum thus consists of a discrete set of monochromatic frequencies, the number of which is finite and is further reduced when the crystal belongs to a highly symmetric class. The small residue of degrees of freedom not included in this description appears as quasi-elastic vibrations having specifiable low frequencies.

New paths in crystal physics

The vast majority of actual solids are crystalline in their ultimate structure. Hence arises the theoretical and practical importance of the subject of crystal physics, and the need for a correct understanding of its fundamental principles. The outstanding feature of the crystalline state of matter is the three-dimensional periodicity of the structure of a crystal, which consists of a great number of similar, similarly situated and oriented groups of atoms, thereby securing for it the fundamental property of physical homogeneity. The size of the individual units or lattice cells of the structure is, in general, of extreme smallness in comparison with the overall dimensions of a macroscopic crystal. It follows as a consequence that the characteristic physical properties of a crystal are determined by its lattice structure and that the form or extension of its exterior boundary is a matter of complete indifference, so long as the crystal is of macroscopic dimensions. These considerations are so little controversial that the need for stressing them here requires explanation. The mathematical physicists of the nineteenth century were so largely concerned with the so-called “boundary value problems” that the tendency has grown up of regarding every physical question needing theoretical treatment as a “boundary value problem” and trying to set up “boundary conditions” for its solution irrespective of whether such considerations are relevant to the problem or not. The subject of crystal physics has in particular suffered from this tradition inherited from an earlier epoch, so much so that theories resting on it continue to be believed in despite their being in total contradiction with the experimental facts. It is proposed in this report to consider a fundamental topic in crystal physics in which such a situation exists, viz., the nature of the vibration spectrum of a crystal lattice. A similar situation has also arisen in a related subject of scarcely less importance, namely, the electronic energy levels of a crystal lattice, but this will be dealt with on a later occasion.

The atomic vibration spectrum

The frequencies of vibration of the atoms in a crystal about their positions of equilibrium in the space lattice lie in the infra-red and may be made accessible to study by various spectroscopic methods. It is evident that the frequency spectrum of the atomic vibrations thus made observable is a characteristic physical property of the crystal. The problem of ascertaining it is in many respects similar

to that of finding the vibration spectrum of a polyatomic molecule and can be handled by very similar methods. For this purpose, we consider the equations of motion of the atoms contained in the unit cell of the crystal lattice. If there are p atoms in the unit cell, there would be $3p$ equations of motion to be solved. The equations would contain the displacements of the atoms included in the unit cell under consideration, as also the displacements of the atoms in the surrounding cells which influence the motion of the former. The equations of motion of the atoms included in these other cells must also be simultaneously satisfied. The relations which must subsist between the various atomic displacements for this to be possible are indicated by the following considerations. Firstly, we remark that as a consequence of the translational symmetry of the crystal, a normal mode of vibration must remain as such when the crystal lattice is given a unit displacement along any one of the three axes of the space lattice. Secondly, we recall the fundamental property of a normal mode that all the particles of the system vibrate with the same frequency and pass simultaneously through their positions of equilibrium, so that the phases of vibration are all either the same or opposite. Combining these two propositions, it follows that the amplitudes of vibration of equivalent atoms remain the same, while the phases either all remain the same or else are all reversed as the result of the unit translation. In other words, in a normal mode, equivalent atoms have the same amplitudes, and either all the same phase or alternately opposite phases of vibration in successive cells along each axis of the lattice. Thus two alternative possibilities arise in respect of each of the three axes, and since they are independent, we have $2 \times 2 \times 2$ or 8 distinct possibilities to be considered. For each of these 8 possibilities we have $3p$ equations of motion involving only $3p$ unknown co-ordinates, and hence capable of being completely solved. Thus in all we have $8 \times 3p$ or $24p$ solutions, which after excluding the three simple translations of the unit cells give us $(24p - 3)$ distinct normal modes of vibration of the crystal lattice.

The foregoing considerations are, of course, purely classical, but their validity is re-inforced when we consider the problem in the light of the general principles of the quantum theory. For this purpose, we may take the case of a crystal the unit cells of which contain each one molecule composed of p atoms linked together. In the absence of interactions, the $3p$ degrees of freedom of the atoms in the cell appear as the 3 translations and $(3p - 3)$ quantised rotations and vibrations of the molecule. Neighbouring molecules having the same frequency would have the same energy and therefore the same amplitude of vibration, but their phases would be uncorrelated. The interactions would however result in specific phase relations being set up and also influence the common frequencies of vibration in a manner determined by the phase relations thus arising. A common frequency of vibration involves a homogeneous set of phase relations throughout the assembly, and, on the basis that the phases are either the same or opposite, there are just 8 possible ways in which they could be arranged. Accordingly, each mode of vibration of the individual molecule would split up into 8 distinct modes of

vibration of the assembly. Assuming that the interactions are strong enough to prevent free rotations of the molecules, we thus obtain $(24p - 3)$ distinct quantised modes of vibration of the assembly. Each of these, of course, must be regarded as being very highly degenerate.

Remarks on some earlier theories

The result thus emerges that the vibration spectrum of a crystal lattice is a discrete line spectrum exhibiting a finite set of monochromatic frequencies. The number of discrete frequencies would be further diminished if the crystal has additional symmetry properties, since several of the distinct normal modes would then have identical frequencies. We may mention a few cases by way of example. A simple face-centred or body-centred cubic lattice would have 4 distinct frequencies of atomic vibration, the diamond lattice would have 8 distinct frequencies and the rock-salt lattice would have 9 such. The modes of vibration in such simple cases can be fully described on the basis of symmetry considerations alone. More generally, however, a detailed investigation would be necessary to find the exact nature of the individual normal modes.

The whole of the present generation of physicists has been brought up to believe in the notion first put forward by Debye in 1912 that the thermal energy of a crystalline solid may be identified with the energy of vibrations of the elastic solid type occurring in it. This idea leads to the result that the frequency spectrum of the atomic vibrations in the crystal is a continuous one, in striking contrast with the conclusions reached above, which indicate that even for the simplest crystals it is a discrete line spectrum of monochromatic frequencies. The reasons for this discrepancy are not far to seek and are, in fact, to be found in the essential illegitimacy of Debye's assumptions. The fact that the specific heat of every crystal attains the value given by the law of atomic heats when its temperature is sufficiently raised, as well as the actual course of the curve by which this value is reached clearly show that we are concerned with the vibrations of the individual atoms in the crystal and that the problem is therefore essentially one of particle dynamics and not one of wave propagation in a continuous solid. Further, the frequencies of vibration which determine the course of the specific heat curve lie, for the most part, well beyond the range where the theory of wave-propagation in an elastic solid can with any show of justification be regarded as applicable. This is readily seen from Debye's own calculations which indicate that by far the largest proportion of his "waves" have lengths of the same order of magnitude as the lattice spacings of the crystal. The invalidity of the Debye theory becomes clearest when we examine the question of "counting" up the modes of vibration of the system. "Waves" as such are not enumerable, since they may be assigned any arbitrary wavelength and consequently arbitrary frequency. Hence, a count of them is meaningless unless it can be shown that only certain discrete wavelengths

with correspondingly defined frequencies are allowed and that all the others are excluded by the very nature of the case, thereby enabling the vibrations to be identified with the normal modes of the system which are enumerable according to Lagrange's fundamental theorem. It is not possible to escape this difficulty by regarding the waves as equivalent to "stationary vibrations" in an elastic solid continuum, since we are principally concerned with vibrations of such high frequency that the lattice structure of the crystal is of the very essence of the problem.

Difficulties of the same kind arise in an even more acute form when we proceed to examine the logical foundations of the theory of lattice vibrations in crystals developed by Max Born and his school. The whole framework of the Born theory rests upon the idea that, since the "boundary conditions" cannot be specified, something should be found which could replace them and by which the fundamental difficulty may be overcome of enumerating the "waves" with which the vibrations of the system are identified. The postulate of the cyclic lattice is introduced in the theory with this object. It provides the requisite number of "waves" whose lengths determine both the so-called acoustic and optical oscillations of the lattice. As in the Debye theory, the "waves" thus chosen are most numerous in the region of wavelengths nearly comparable with the lattice spacings of the crystal, with the result that both the "acoustic" and "optical" vibrations are spread out into "branches" extending over a wide range of frequencies—as is indicated by the calculations made by the Born school for the few cases in which the ideas have actually been worked out.

The artificial character of the cyclic postulate is very obvious, and it is sufficient to point out that it does not achieve the purpose for which it has been introduced. Born's own equations show that, if the vibrations of the medium are regarded as waves, then the wavelengths can be chosen quite arbitrarily. Unless therefore it can be shown that the particular choice made is uniquely demanded by physical reasoning—which is necessary if the resulting motion is to be identified with normal vibrations in the Lagrangian sense—the frequency spectrum determined by such arbitrary choice of wavelengths can have no possible physical meaning or significance. Indeed, it is plain that the "waves" of the Born theory have no claim whatever to be regarded as the normal modes of vibration of the crystal lattice.

Experimental configuration of the new ideas

The theoretical result that the vibration spectrum of a crystal lattice is a discrete or line spectrum of monochromatic frequencies is naturally subject to the restrictions implied in its derivation. The theory is based on a consideration of small oscillations under harmonic forces in an ideal lattice. Departures from perfect monochromatism of the vibrations are naturally to be expected when these simplifying restrictions are removed, viz., when we consider oscillations of

finite amplitudes, anharmonic forces and crystal lattices which are imperfect or which are disturbed appreciably by thermal agitation. These may be minimised by working under appropriate conditions, and the most decisive results are naturally those obtained with crystals most nearly approaching ideality and held at a sufficiently low temperature. Various methods of investigation are available, viz., the spectra of light-scattering, luminiscence and absorption in crystals and a vast array of experimental evidence gathered during the last two decades by these and other methods of exact spectroscopic research is on record, to which the interested reader may be referred.

Of special interest are the recent investigations of Dr R S Krishnan (*Nature*, **159**, 60, 1947) on the scattering of light in diamond observed under high resolving powers which give a direct objective demonstration of the monochromatic character of the atomic vibrations in that crystal and simultaneously furnish an experimental refutation of the ideas underlying the older theories. Analogous studies with various other crystals, viz., rock-salt, ammonium chloride, ammonium bromide, corundum, topaz etc., have also been carried out by Dr R S Krishnan and the results obtained by him are particularly significant in view of the fact that they have been carried out under critical experimental conditions, viz., using the highest possible spectroscopic resolving powers and also working with the crystals held at a series of temperatures down to that of liquid air. The detailed results of these investigations will shortly be published as a Symposium on the Vibration Spectra of Crystal Lattices by the Indian Academy of Sciences, which will also include a complete review and theoretical discussion of the entire body of spectroscopic evidence available up to date from the most exact investigations on the behaviour of crystals made by investigators in various countries. It emerges unequivocally from these studies that the theories which suggest that the atomic vibrations in crystal lattices give a continuous spectrum are in clear contradiction with the experimental facts and are therefore wholly unsustainable.

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The vibration spectra of crystals—Part I. Basic theory

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1. Introduction

A knowledge of the modes and frequencies of vibration of the atoms in a crystal about their positions of equilibrium is of the utmost significance for the theory of the solid state. For, such knowledge is complementary to that regarding the structure of the solid furnished by the data of X-ray and electron diffraction. These latter data enable the geometric positions of the atoms to be ascertained, while the modes and frequencies of atomic vibration permit of the evaluation of the forces which hold them together as a rigid structure. The study and interpretation of the vibration spectra of crystals is thus the pathway to a fuller understanding of the nature of the solid state and the elucidation of the physical properties of solids generally. It follows that the theory of these spectra is a topic of outstanding importance for the progress of crystal physics.

The problem of finding the nature of the vibration spectrum of a crystal may be approached from two different points of view. The first is that which bases itself on the known behaviour of elastic solids. Acoustic theory and experience alike indicate that a solid body has a whole series of normal modes of vibration determined by its external form and dimensions. These may be regarded as stationary vibration patterns resulting from the interference of elastic waves

which traverse the interior of the solid in different directions and suffer reflections at its outer boundary. On this view, the frequencies of the modes would be determined by the length of the waves and their type. The problem of enumerating the possible stationary vibrations and of arranging them in a frequency scale is somewhat more complicated than the analogous problem for an enclosed volume of fluid, since there are three types of waves instead of one as in the latter case, and since the wave-velocities in a crystal also depend on the direction of propagation. It is evident, however, that the general nature of the results would be similar in the two cases. There would be a crowding together of the modes as the wavelengths are diminished and the frequencies of vibration are correspondingly greater, their number becoming ultimately very large. Hence, the vibration spectrum would to all intents and purposes be a continuous one. It may be remarked that the method of enumeration of the vibrational modes in this manner according to wavelengths or frequencies does not in any way compel us to take account of the discrete structure of the medium and in effect regards the latter as a continuum.

The second point of view from which the subject may be approached is that in which we fix our attention on the movements of the individual atoms in the solid. The structure of a crystal is built up of a great number of units of very small size, all of which are exactly alike and each of which comprises a finite number of atoms. Since the range of the interatomic forces is also very small, the problem of finding the possible modes of vibration of these groups of atoms is of the same general nature as that of finding the normal modes of vibration of a polyatomic molecule. The nature of the results to be expected would therefore also be similar, and the vibration spectrum of a crystal should accordingly consist of a finite set of sharply defined frequencies, each of which represents an exactly specifiable mode of vibration. The characteristic frequencies would be the same for every one of the vibrating groups of atoms, and hence in relation to the entire crystal must be considered as being highly degenerate.

Thus, the continuum standpoint and the atomistic standpoint lead to conceptions of the nature of the vibration spectrum of a crystal which are radically different from each other. The two points of view are therefore mutually exclusive, and since they both appear reasonable, we infer that the ranges of frequency in which they are respectively appropriate are quite different. The continuum standpoint is the one which would naturally be adopted in considering the lower part of the frequency range comprised in the spectrum, while the atomistic standpoint is obviously the correct one to take up when we are concerned with the upper part of the frequency range. In other words, the vibration spectrum of every crystal is composed of two parts which are essentially different in nature, namely the atomic vibration spectrum properly so called which exhibits a discrete set of monochromatic frequencies appearing in the infra-red, and the elastic spectrum which is continuous and forms a low-frequency appendage to it.

The present paper has a two-fold purpose. In the first part, we shall present a theoretical discussion of the problem and justify the statements made above concerning the nature of the vibration spectra of crystals. The arguments put forward are simpler without being less rigorous than those contained in an earlier presentation of this topic (Raman 1943). In the later parts, we shall review the experimental data for the spectroscopic behaviour of crystals as known at the present time and show that the facts are in complete accord with the theoretical ideas developed in the first part. Incidentally, we shall also comment upon the older theories of the subject which lead to the conclusion that the vibration spectrum of a crystal is a continuous one throughout the entire range of frequency. It will be shown that these theories are based on an extrapolation of the ideas derived from elastic solid behaviour into the atomistic field, and that such extrapolation is invalid and leads to results which are contradicted by the experimental facts.

2. The eigenvibrations of crystal structures

The structure of a crystal consists of a great number of similar and similarly situated cells each containing the same number of atoms, and the clue to the spectroscopic behaviour of the crystal is therefore to be found in the properties of the group of atoms contained in the unit cell. In other words, we have to consider the possible modes of vibration of the group of atoms included in the unit cell, and the problem is therefore generally analogous to the theory of vibrations of polyatomic molecules. There is however a notable difference between the two cases arising from the fact that the atoms in the unit cell are not isolated from the rest of the crystal; it is clearly necessary to take account of the interactions with the surrounding cells in so far as they affect the motion of the atoms in the cell under consideration. The frequencies of vibration with which we are concerned lie in the infra-red. Hence, the problem does not lie strictly within the scope of the classical mechanics. Nevertheless, as in the case of polyatomic molecules, we may hope that the methods of classical mechanics suffice to yield results which are in agreement with the facts in all essential respects. Also, as in the case of polyatomic molecules, we may in the first instance limit ourselves to the theory of small vibrations under harmonic forces. The modifications arising from the removal of these restrictions are, however, by no means unimportant. They will be dealt with later in the paper.

In any eigenvibration of the atoms contained in the unit cell, their frequencies of vibration are necessarily the same, while the phases are all the same or opposite. In considering the interactions with the surrounding atoms, we may properly assume that this is true also for the atoms included in the surrounding cells whose direct interactions with the unit cell under consideration are of

sensible magnitude. We proceed to find the cases for which these requirements are satisfied.

The equations of motion of the atoms in a crystal for an oscillation proportional to $\sin \omega t$ take the general form

$$m_k \xi_{kr} \omega^2 = \sum_s \sum_l \sum_\eta F_{\eta ls}^{\xi kr} \cdot \eta_{ls}. \quad (1)$$

Here, m denotes the mass of an atom, while the co-ordinates ξ , η , ζ indicate its displacements parallel to x , y and z respectively. The suffixes k and l indicate particular atoms in the unit cell, where the suffixes r and s refer to particular cells of the lattice in which the atoms are situated. F denotes a force-factor, its upper and lower suffixes indicating respectively the displacement of the particular atom on which it acts and the displacement of the particular atom giving rise to the force. The triple summation must be made over the ξ , η and ζ values of all the atoms in the crystal for which the force-factors are not negligible in respect of the particular atom under consideration; the size of the domain including all such atoms would depend on the range of the interatomic forces. We shall assume the crystal to be of sufficient size to ensure that its external boundary is very remote from the limits of such domain. To enable us to solve the set of $3p$ equations of motion of the p atoms comprised in the unit cell under consideration, we shall require to know the displacements of the atoms in the neighbouring cells which also appear on the right-hand side of the equations (1). To enable them to be found, we make use of the fact that in any eigenvibration, the equations of motion of the atoms included in these cells must also simultaneously be satisfied. Considering the atoms comprised in a cell adjacent to the r th which we denote as the $(r + 1)$ th, their equations of motion would have the form

$$m_k \xi_{k(r+1)} \omega^2 = \sum_s \sum_l \sum_\eta F_{\eta l(s+1)}^{\xi k(r+1)} \cdot \eta_{l(s+1)}, \quad (2)$$

the cell index $(s + 1)$ representing one adjacent to the cell of index s along the same axis is as that on which the r th and $(r + 1)$ th cells are situated.

Now the transitional symmetry of the crystal has the consequence that the force-constants for adjacent cells satisfy general relations of the form

$$F_{\eta ls}^{\xi kr} = F_{\eta l(s+1)}^{\xi k(r+1)}. \quad (3)$$

Comparing equations (1) and (2) and taking account of the relations given by (3), we notice that provided general relations subsist connecting the displacement of equivalent atoms which are *either of the form*

$$\xi_{kr} = \xi_{k(r+1)} \quad \text{and} \quad \eta_{ls} = \eta_{l(s+1)} \quad (4)$$

or of the form

$$\xi_{kr} = -\xi_{k(r+1)} \quad \text{and} \quad \eta_{ls} = -\eta_{l(s+1)}, \quad (5)$$

the $3p$ equations (1) and the corresponding $3p$ equations (2) would become identical. In these circumstances, any set of displacement co-ordinates which satisfy the former set of equations would also satisfy the latter. Further, the number of unknown co-ordinates appearing in the $3p$ equations (1) would be reduced to $3p$ only by reason of (4) or (5), thus enabling them to be completely solved. However, (4) and (5) being different alternatives, the $3p$ equations obtained by making use of these relations would be different, and the solutions obtained would also be different. Further, there would be two such alternatives in respect of the cells adjacent to each other along each of the three axes of the lattice, and these three sets of alternative possibilities would be independent of each other, so that there would be $2 \times 2 \times 2$ or 8 sets of alternative possibilities to be considered. Each of these would, in general, give a different set of $3p$ equations and therefore a different set of solutions. Thus, in all, we would obtain $24p$ solutions on the basis of the relations indicated by (4) and (5) above.

We shall now consider the significance of the alternative relations (4) and (5) which we have assumed to subsist in order to enable the equations of motion to be reduced and solved. They evidently signify that the *amplitudes of vibration of equivalent atoms in the different cells are the same, while their phases are either all the same or else alternate in successive cells along each of the three axes of the lattice*. In either case, the energy of vibration is the same in the different cells of the lattice when the frequency is the same. It is obvious that such a state of affairs necessarily represents a possible stationary regime within the crystal. In other words, the $24p$ solutions of the equations of motion obtained on this basis represent the normal modes of vibration of the crystal structure. It will be noticed that only in $3p$ solutions would the phase of the vibration be the same in all the cells of the lattice; in the remaining $21p$ solutions, the phase of the vibration is opposite in adjacent cells of the lattice along one, two or all three of its axes. In these latter, the condition that the centre of inertia of the system should remain at rest is automatically secured. The constraints necessary to secure the same condition would however reduce the $3p$ solutions of the former kind to $(3p - 3)$ solutions, so that in all we would have $(24p - 3)$ eigenvibrations and not $24p$.

It will be noticed that if we mark out domains in the crystal which extend in each direction twice as much as the unit cells of the lattice, the pattern of vibration within each such domain would be the same as for neighbouring ones in each of the $(24p - 3)$ modes of vibration indicated by the preceding argument. *Hence, the results of that argument may be summarised by the statement that the units of the vibration pattern of the crystal are super-cells having twice the linear dimensions and therefore eight times the volume of the static units of the crystal structure*. The number of atoms included in each such dynamic unit or super-cell is $8p$, and we may therefore regard the $(24p - 3)$ modes as its internal vibrations and the three excluded degrees of freedom as its three translations. This point of view is useful in two ways. Firstly, it indicates that in relation to the entire crystal, *each of our $(24p - 3)$ modes of vibration is highly degenerate, being in fact N -fold degenerate if N be*

the number of super-cells contained in the crystal. Secondly, the three excluded degrees of freedom which represent the translations of the super-cell provide an appropriate starting point for a consideration of the possible elastic modes of vibrations of the solid. We shall return to this aspect of the subject later in the paper.

3. Some illustrative examples

As an illustration of the general theory set out above, we shall now consider two specific cases, viz., that of a face-centred cubic lattice of atoms, as also the structure resulting from the interpenetration of two such lattices, viz., that of diamond or zinc-blende and describe their characteristic modes of vibration.

The unit cells in a face-centred cubic lattice are really rhombohedra, the unit translations being those by which an atom placed at the corner of the cube goes over respectively to the three neighbouring face-centred atoms. The theorem that equivalent atoms in the lattice have the same amplitude of vibration and either the same phase or the opposite phases successively along the axes of the lattice enables us immediately to describe the possible modes. An atom located at a cube corner and the three others located at the nearest face-centres form the four vertices of a regular tetrahedron the faces of which are the (111) planes, while its diagonal planes are the (100) planes of atoms in the crystal. It is easily seen that all the eigenvibrations are movements of these planes of atoms; alternate planes move in opposite phases, while the directions of movement are indicated by considerations of symmetry to be either normal or tangential to the respective planes. Thus, there are only four different kinds of vibration of the lattice, namely the normal and tangential vibrations respectively of the octahedral and cubic planes of atoms, the tangential vibrations being twice as many as the normal ones. As there are four sets of octahedral planes and three sets of cubic planes in the lattice, the four species of vibration have degeneracies of 4, 8, 3 and 6 respectively, making up a total of 21 modes. Adding the 3 translations of the super-lattice cell, we obtain the total of 24 degrees of freedom of the 8 atoms contained in it.

The possible modes of vibration of the diamond or zinc-blende structure may be obtained by coupling similar modes of vibration of the two face-centred lattices as described above with appropriate relations of amplitude and phase. There are only two possibilities, viz., that the oscillations of the planes of atoms adjacent to each other belonging respectively to the two lattices are in the same or the opposite phase. Hence, the four types of eigenvibration of a face-centred cubic lattice give us eight types of vibration of the structure. To this, we must add a ninth mode of vibration representing the translations in opposite phases of the two lattices with respect to each other. Thus in all, we have 9 modes with degeneracies 4, 4, 8, 8, 3, 3, 6, 6 and 3 respectively, making up a total of 45 degrees of freedom. The 3 translations of the two lattices moving together in the same

phase are excluded from this scheme. Taking account of them, we recover the 48 degrees of freedom of the 16 atoms included in the super-lattice cell.

4. The elastic vibration spectrum

We now turn to a consideration of the problem from the point of view provided by the theory of the vibrations of elastic solids. The principles on which an enumeration of the possible modes of vibration of an elastic solid may be based are indicated by the comparatively simpler problem of the vibrations of an enclosed volume of fluid. Considering a rectangular chamber whose edge-lengths are α , β , γ respectively, it may be shown either directly or by application of Fourier's theorem that the general solution which includes all particular solutions of the equations of wave-motion satisfying the boundary conditions at the walls of the enclosure is

$$\phi = \sum \sum \sum (A \cos kat + B \sin kat) \times \cos \frac{n_1 \pi x}{\alpha} \cos \frac{n_2 \pi y}{\beta} \cos \frac{n_3 \pi z}{\gamma}, \quad (6)$$

where ϕ is the velocity-potential, A and B are arbitrary constants, while n_1, n_2, n_3 are positive integers and k is $2\pi/\lambda$, where λ is the "wavelength" of the stationary vibration. It is defined by the relation

$$k^2 = \pi^2(n_1^2/\alpha^2 + n_2^2/\beta^2 + n_3^2/\gamma^2), \quad (7)$$

and hence λ diminishes as n_1, n_2, n_3 are increased. If the medium be regarded as continuous, n_1, n_2, n_3 may be as large as we please, and the number of possible stationary wave-patterns is then unlimited. We may, however, if we so desire, set a limit to the total number of possible stationary patterns of vibration by assuming that the maximum possible values of n_1, n_2, n_3 are respectively N_1, N_2, N_3 . The total number of possible eigenvibrations is then the product $N_1 N_2 N_3$.

Equation (7) connects the "wavelength" of an oscillation with the linear dimensions of the vibrating body and the number of parts of its aliquot division by the resulting vibration in each of three mutually orthogonal directions. We shall not be wholly at fault in assuming a similar relationship to subsist in the case of the elastic vibrations of a rectangular block of solid. Earlier in the paper, we have seen that the atomistic approach to our problem leads to the result that the structure of a crystal has $(24p - 3)$ characteristic modes of vibration, and we identified these with the internal vibrations of a group of $8p$ atoms included in a super-lattice cell having twice the linear dimensions and hence eight times the volume of the unit cell of the crystal lattice. The three excluded degrees of freedom on the same basis represent the three translations of the super-cell, and if there be N such super-cells comprised in the entire crystal, we have $3N$ degrees of

dynamical freedom of movement which are left unaccounted for in the atomistic treatment. In view of the remarks made in the introduction, we may properly identify these with the total number of possible elastic eigenvibrations of the crystal. Since there are three types of elastic waves in a crystal, we may ascribe one-third of the total number to each of the corresponding types of elastic eigenvibration. Accordingly, on the basis of the foregoing argument, we set

$$N = N_1 N_2 N_3, \quad (8)$$

which signifies merely that the total number of elastic eigenvibrations of each type is the same as the total number of super-lattice cells comprised in the crystal. By virtue of (8), we may write (7) in the form

$$4/\lambda^2 = (n_1^2/N_1^2 \cdot 1/d_1^2 + n_2^2/N_2^2 \cdot 1/d_2^2 + n_3^2/N_3^2 \cdot 1/d_3^2), \quad (9)$$

which connects the reciprocal of the wavelength λ of the vibration with the reciprocals of certain spacings d_1, d_2, d_3 whose product $d_1 d_2 d_3$ is equal to the volume of the super-lattice cell. As N_1, N_2, N_3 are very large numbers, the wavelengths permitted by (9) form a practically continuous sequence of values which become densely crowded together as n_1, n_2, n_3 approach their maximum possible values N_1, N_2, N_3 . When one of the three numbers n_1, n_2, n_3 has its maximum value and the other two are set equal to zero, λ becomes equal to $2d_1$ or $2d_2$ or $2d_3$ respectively. Thus, the "limiting wavelengths" along the three edges of the rectangular block are related in a very simple manner to the linear dimensions of the super-lattice cell of the crystal structure. In the particular case where the edges of the block are parallel to the axes of the crystal lattice, *the limiting wavelengths are just twice the edges of the super-lattice cell or four times the edges of the lattice cell of the crystal*. Vice versa, if the limiting wavelengths of the elastic eigenvibrations are so chosen as to satisfy these relation, *the number of degrees of dynamical freedom left out from the atomistic enumeration of the vibrations in the crystal are completely accounted for as its elastic eigenvibrations*. It will be noticed that we are *not* assuming $d_1 = d_2 = d_3$, and hence the argument is not limited to the case of cubic symmetry but is more general. In passing from an enumeration of the eigenvibrations on the scale of wavelengths provided by (9) to an enumeration on a scale of frequencies, we must, of course, take account of the fact that the ratio of wavelength to frequency, is different for the three types of elastic waves and is also a function of the direction of propagation.

We may illustrate the preceding argument by considering once again the case of a face-centred cubic lattice. As mentioned earlier, the eigenvibrations of such a lattice are of four different kinds which may be described as being respectively normal and tangential oscillations of the cubic and octahedral planes of atoms, the movements of alternate planes of atoms being in opposite phases. The normal oscillations of the cubic planes are represented in figure 1. A similar figure with the arrows parallel to the atomic planes would represent the tangential

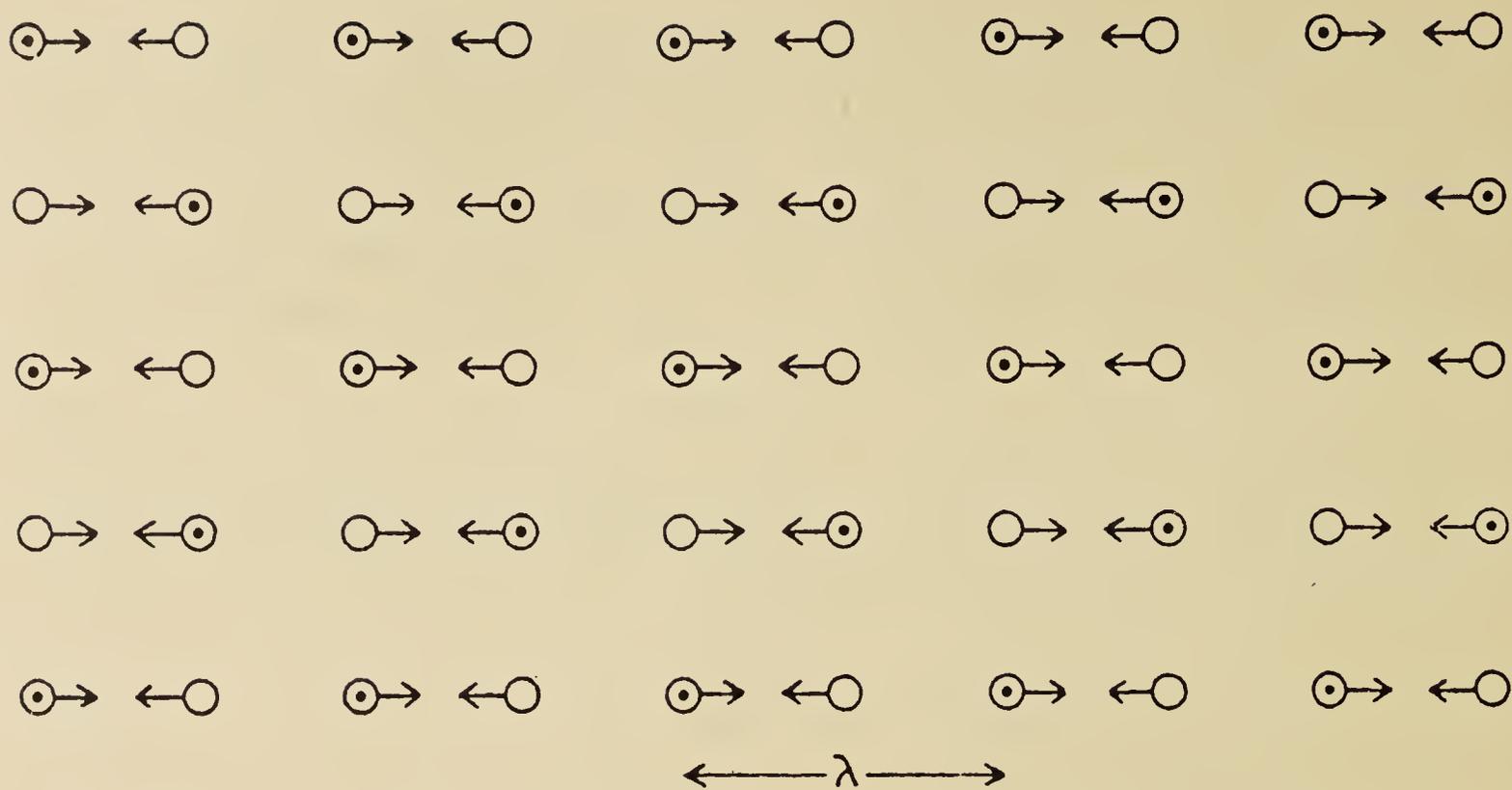


Figure 1. Eigenvibrations of a face-centred cubic lattice.

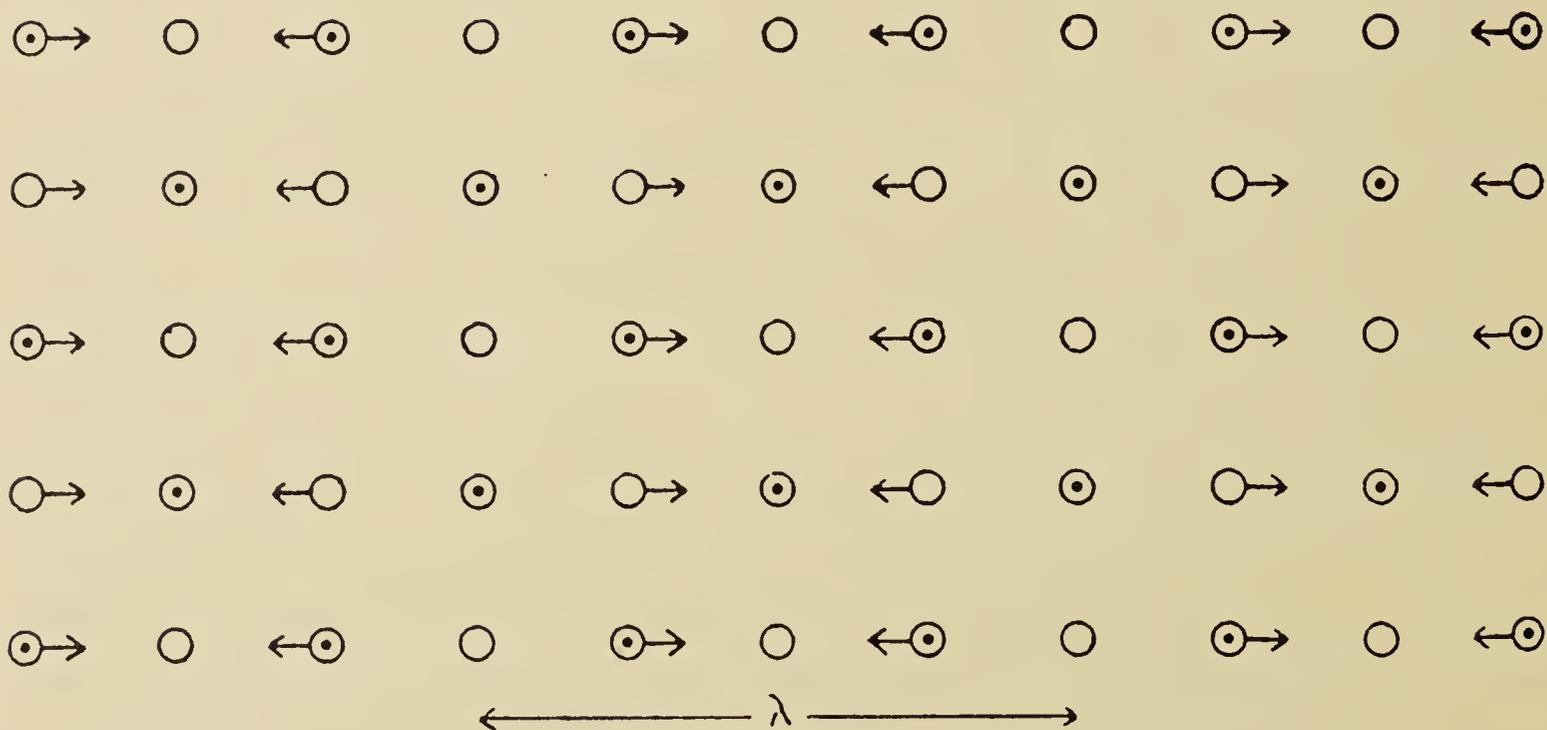


Figure 2. Elastic vibrations of minimum wavelength in a face-centred cubic lattice.

oscillations. With an altered spacing of the planes the figure would also represent the oscillations of the octahedral layers of atoms.

As will be seen from the figure, there are no nodal planes or layers of atoms at rest, and since the nature of the vibration is completely determined by the lattice structure, the mode is a characteristic property of that structure and not an elastic vibration properly so called. Since, however, the motion repeats itself periodically along the crystal axes, we may ascribe to it a "wavelength" which as seen from the

figure is *twice* the distance between the atomic layers. Figure 2 represents an elastic vibration properly so-called with the smallest possible wavelength; every alternate layer of atoms is a nodal plane which remains at rest, while the intervening planes of atoms move in opposite phases. The “wavelength” is thus four times the distance between the atomic layers. A similar figure with the arrows parallel to the atomic planes would represent the transverse elastic vibration of smallest wavelength.

We can, of course, similarly picture elastic vibrations in which every third or fourth or fifth plane of atoms is at rest, while the intervening planes of atoms oscillate with phases which are opposite on either side of each nodal plane. The “wavelengths” of such oscillations would be respectively 6, 8 or 10 times the spacing of the atomic planes, the motion repeating itself at these intervals and the energy of the vibration being the same in the successive layers separated by the nodal planes. Such an arithmetical progression of increasing wavelengths is however altogether different from that contemplated by equation (9) above in which they form a densely crowded sequence with wavelengths diminishing in harmonic progression, the permitted values being determined by aliquot division of the macroscopic dimensions of the solid. Moreover, the form and disposition of the nodal planes of elastic vibration are determined by the shape and dimensions of the outer boundary of the solid and not by its internal structure. Hence, having set the lower limit of wavelength at four times the lattice spacings, we must for all larger wavelengths and therefore lower frequencies of elastic vibration ignore the discrete structure of the solid and treat it as a continuum. *Per contra*, we are precluded from extending into the region of the higher frequencies of vibration a treatment based on the idea of free propagation of elastic waves of lengths determined by the external dimensions of the solid.

5. Remarks on some earlier theories

The Debye theory—The foregoing remarks prepare us for a consideration of the earlier theories of the vibration spectra of crystals. The prototype of these theories is Debye’s well known treatment (1912) of the specific heat problem for elementary solids. This is based on the postulate that the thermal agitation in a solid may be identified with stationary elastic vibrations in it of various wavelengths superposed on each other. All the three possible kinds of elastic vibration are assumed to have frequencies inversely proportional to their respective wavelengths and to terminate at a common upper limit of frequency. The simplicity of the Debye formula for the specific heat is a consequence of these specific assumptions. Later writers have sought to modify the theory by postulating that all the three types of elastic vibration (one longitudinal and two transverse) have a common upper limit of wavelength instead of frequency. With this modification, the Debye theory and the results derived in the preceding

section may be readily compared with each other. Limiting ourselves to the case in which each cell of the crystal lattice contains only one atom, it is obvious that if all the possible atomic vibrations are considered as elastic eigenvibrations, they would be eight times more numerous, and the limiting wavelengths would be one-half of those derived in the present paper. The additional eigenvibrations are those having the smallest wavelengths and therefore the highest frequencies, and they form the great majority, viz., seven out of every eight.

In order to appreciate the precise nature of the situation thus arising, we consider the specific case of a face-centred cubic lattice. Figures 1 and 2 above show respectively the characteristic eigenvibrations of the structure and the elastic vibrations of minimum wavelength possible in it according to our present point of view. It is evident that the great majority of the stationary vibrations assumed by the Debye theory (seven-eighths of the total number) would have "wavelengths" intermediate between those represented by these two figures. We may remark, however, that a characteristic feature of stationary vibrations in a continuous elastic medium—*vide* equation (6) of the preceding section—is that the medium is partitioned by the nodal planes into cells in which the energy of oscillation is the same and the phase opposite in alternate cells. The same situation in the case of a discontinuous periodic structure is represented in figures 1 and 2, but there is clearly no possibility of a stationary vibration with these characters and of wavelength intermediate between twice and four times the atomic spacing. We can, of course, postulate waves of any intermediate wavelength that we may choose and assume them to traverse the discontinuous periodic structure in opposite directions. But the result of their superposition would in no way resemble the stationary vibrations described in equation (6) which form the basis of the enumeration, since the energy of the vibration would fluctuate arbitrarily along the direction of propagation. The situation is thus that *the overwhelming majority of the stationary modes of vibration which are assumed to exist in Debye's theory are possible only in an elastic continuum but have no counterparts in a periodically stratified structure.* In other words, the Debye theory is based on an extrapolation of notions derived from the behaviour of elastic solids into the field of atomic theory, such extrapolation being, on the face of it, physically untenable. The postulates made in the theory are therefore invalid even in the case of crystals of the simplest structure to which the foregoing discussion has been limited.

The Born-Karman theory—We now proceed to comment on the so-called lattice dynamics of Born and Karman. This claims to be more exact than the Debye theory and also to include within its scope crystals of complex structure comprising two or more atoms in each lattice cell. For this purpose, the theory (1923) divides the degrees of freedom of the system—namely thrice the total number of atoms—into distinct groups which are each equal to the number of lattice cells comprised in the crystal. Each degree of freedom corresponds to a

wave which is assumed to traverse the crystal, and we have thus present in it an immense number of sets of waves of different wavelengths, each set corresponding to a group of wavelengths chosen and allotted on the same common plan. $(3p - 3)$ of the groups of waves represent the so-called "optical" vibrations of the lattice, while the remaining 3 groups represent its "acoustic vibrations". The frequencies of vibration depend on the wavelengths, and each group accordingly represents an immense number of different frequencies of vibration. The nature of the vibration spectrum has to be determined by calculation on the basis of specific assumptions regarding the nature and magnitude of the interatomic forces. As the computations are laborious, it is not surprising that comparatively few cases have actually been worked out in detail. The published results, however, indicate that the vibration spectra in both the "optical" and the "acoustic" branches are diffuse continua which overlap each other (Blackman 1935; Kellermann 1940). Such a result might have been expected a priori in view of the assumptions underlying the theory. For the "wavelengths" assumed are most crowded together when they are smallest and are most nearly comparable with the lattice spacings of the crystal. The "optical frequencies" depend notably on the wavelengths when these are small, and hence the assumed distribution of wavelengths results in spreading out the "optical spectrum" into a diffuse continuum, instead of its being a set of sharply defined lines as in the case of vibration spectra of polyatomic molecules.

The Born–Karman theory rests on the premise that a crystal has as many different frequencies of vibration as it has degrees of dynamical freedom, and the sets of waves with which its vibrations are identified are indeed assumed to secure this result. Neither the premise nor the assumptions made to ensure its fulfilment can, however, be justified. As has been remarked earlier in the paper, a crystal consists of an immense number of similar groups of atoms whose characteristic modes of vibration are necessarily all similar, and hence a high degree of degeneracy is necessarily to be expected in respect of the vibration frequencies of the system. Further, *a wave is not a normal vibration since the phase changes progressively along its course*. Hence, an enumeration of waves is not a valid procedure unless it can be shown that a physical mechanism exists which selects particular wavelengths and transforms the motion to normal vibrations of a determinate type. Such a mechanism exists in respect of the elastic vibrations, being provided by the reflection of the waves at the boundaries of the crystal and the consequent formation of wave-patterns of a determinate type by interference. But as we have seen above, stationary wave-patterns of this kind can account for only a small proportion of the dynamical degrees of freedom even in the case of crystals of simple type having only one atom in each lattice cell. It follows that in the case of crystals of complex structure, the proportion of the dynamical degrees of freedom represented by stationary wave-patterns would be even smaller. Hence, the identification of the so-called "optical vibrations" with waves having the same set of wavelengths as the elastic vibrations has no physical meaning or justification. In effect, the Born–Karman theory ascribes to the atomic structure

of a crystal an immense number of modes and frequencies of vibration which it does not really possess.

6. Molecular crystals

The arguments and results set out in section 2 above are, of course, quite general, and do not depend on the particular manner in which the p atoms in the unit cell of the crystal are linked with each other or with the atoms in the neighbouring cells. Some of them, for instance, may be constituent parts of ions or molecules, e.g., the CO_3 ions in calcite or the C_{10}H_8 molecules in a naphthalene crystal. Indeed, it is precisely such cases which make it most obvious that the vibration spectra of crystals in the infra-red should consist of a sharply defined set of monochromatic frequencies and not a diffuse continuum. For, we know that the ions or molecules in the free state have sharply defined spectral frequencies; though their mutual interactions in a crystal would have to be considered, these interactions are exactly specifiable and hence could only result in altering the vibration frequencies and increasing their number without changing the essential nature of the spectra. To show that this is the case, we may consider the particular example of a crystal in which the p atoms in each lattice cell form a single molecule. Each such molecule has $3p$ degrees of dynamical freedom which may be identified with specific modes of vibration in the crystal, since simple rotations and translations are excluded, at least ordinarily. The nature of a normal vibration, viz., that all the particles in the system vibrate with the same frequency and with the same or opposite phases enables us to define the manner in which the vibrations of the interacting molecules would be related to each other. Since every molecule vibrates with the same frequency as its neighbours, the forces which come into play must be the same for all. These forces include not only the internal ones arising within each molecule but also the forces of interaction between them. Hence, the latter should also be the same for all molecules. But the forces of interaction are determined by the amplitudes and phases of vibration. Hence, to ensure that the forces of interaction are the same, it is necessary that the molecules which interact with each other vibrate with the same amplitude, while each molecule has the same relation of phase to its neighbours that every other molecule has. The latter requirement can only be satisfied if the phases are either all the same or else alternate in successive cells of the lattice along one, two, or all three of its axes. We have thus $2 \times 2 \times 2$ or 8 different ways in which the requirements for a normal vibration may be satisfied. Hence, each of the $3p$ possible modes of vibration of a molecule would be modified in 8 different ways, giving us in all $24p$ different normal vibrations, which is the same result as that deduced in section 2, if we exclude the 3 translations of the molecules moving together as a group.

The foregoing approach to the subject is useful in elucidating the relations between the vibration spectrum of a crystal and the spectra of the same substance

in the liquid and gaseous conditions. The $(24p - 3)$ modes of vibration may be divided into two classes, namely, $(3p - 3)$ modes in which the amplitude and phase of the vibration of a molecule are the same as those of its neighbours, and $21p$ modes in which the vibration occurs in opposite phase in alternate layers of the crystal structure. The $(3p - 3)$ modes of the first kind represent the internal vibrations and the rotational oscillations of the molecules, while the $21p$ modes of the second kind would include also the 21 modes of translational oscillation of the molecules against each other. Unless the forces of interaction are large, the internal oscillations of the second kind would differ but little in frequency from similar oscillations of the first kind, and both would be nearly the same as for the free molecules. On the other hand, the rotational oscillations with discrete frequencies which are characteristic of the crystal are determined entirely by the interactions between the molecules, and hence they should differ notably in the first and second class of normal modes.

7. Anharmonicity and interaction of vibrations

So far, we have concerned ourselves with small oscillations under harmonic forces. In the actual problem, the amplitudes of vibration are determined by quantum-theoretical considerations and are by no means infinitesimal. Hence, a complete theory would require us to include, in addition to the forces proportional to the atomic displacements, also forces proportional to their squares and to their products. On introducing such additional terms into the equations, it becomes evident that the motion can no longer be described as a summation of independent normal vibrations and that interactions would arise profoundly modifying the dynamical behaviour of the system. Problems of this kind have already been considered in the theory of the vibrations of polyatomic molecules (Herzberg 1945), and we may therefore take over the known results of that theory *mutatis mutandis* in our present case. If the anharmonicity be not too large, the behaviour of the system may still be described by sets of quantum numbers, each set corresponding to one of the normal vibrations possible in the harmonic approximation. The quantum numbers do not, however, as in the harmonic case, represent equal increments of energy, but a diminishing sequence of increments. The selection rules are also modified and in particular, overtones and combinational frequencies forbidden in the harmonic approximation are permitted to appear. Overtones and combinations may also appear by reason of the electric moments associated with the vibrations having a non-linear dependence on the amplitudes. Anharmonicity results further in cases of non-accidental degeneracy in the splitting up of various higher energy levels which would be coincident in the harmonic approximation. Accidental degeneracy may also result in splitting up or displacing the energy levels concerned and in modifying the intensities with which they appear in the spectra.

8. Influence of temperature

Anharmonicity also plays an important role when we consider the effect of elevating the temperature of a crystal on its vibration spectrum. As the temperature rises, a considerable proportion of the various low-lying energy levels would be thermally excited, as also a smaller proportion of the higher ones. Hence, any further excitation caused, for instance, by the incidence of radiation on the crystal has to start from the thermally excited levels, and by reason of the anharmonicity, the energy increments would then be less than for similar transitions from the ground state. As a consequence, the spectral lines corresponding to various possibilities which are equivalent in the harmonic approximation would no longer be coincident. The effect of elevating the temperature would accordingly be to lower the vibrational frequencies and simultaneously to spread them out over a finite range of values. Further, since the majority of the induced transitions start from the thermally excited levels and not from the ground state, the electrical anharmonicity would also come into play and make the observed intensity of the lines less than what they would be if there were no such anharmonicity.

It is evident that similar results would also follow from the interaction between the eigenvibrations of the crystal structure and the elastic vibrations of the solid. The energy of an elastic vibration is distributed over the entire volume of the crystal, and hence its amplitude would be exceedingly small. Hence, the elastic vibrations, considered individually, would have no sensible perturbing effect on the eigenvibrations. The position would however, be altered if we consider the aggregate effect of all the elastic modes of vibration when thermally excited, since their number is very large. A convenient way of regarding the matter is to fix our attention on a very small element of volume in the crystal. This volume element would, as the result of the thermal agitation, suffer fluctuations of density. These may be regarded as oscillations of varying amplitude and frequency. When the volume element considered is sufficiently small, the density fluctuations would be large enough to perturb the eigenfrequencies to an observable extent, lowering them and spreading them out over a finite range of values.

9. Summary

The paper presents the author's theory of the vibration spectra of crystals from a fresh point of view. It is shown that the nature of the spectra is necessarily different in the two regions of frequency in which they represent respectively the characteristic eigenvibrations of the crystal structure and the stationary wave-patterns of elastic vibration. The eigenvibrations repeat themselves in volume elements within the crystal having twice the linear dimensions and eight times the volume of the lattice cells. The number of modes of eigenvibration is $(24p - 3)$, p

being the number of atoms in each lattice cell. The spectral frequencies which are $(24p - 3)$ in number (or less by reason of crystal symmetry) are accordingly monochromatic. In relation to the entire crystal, they are highly degenerate. The three missing degrees of freedom are exactly accounted for when the possible elastic vibrations which give a quasi-continuous spectrum of frequencies are enumerated. The limiting elastic wavelengths come out as four times the lattice spacings of the crystal. The effects of anharmonicity are also considered. It is shown that they result in lowering and spreading out the spectral frequencies of the crystal when its temperature is elevated.

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The vibration spectra of crystals—Part II. The case of diamond

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1. Introduction

Of recent years, there has been a great accession of exact knowledge regarding the spectroscopic behaviour of crystals. Much of this knowledge has been gained by the method of investigation introduced by the present writer in the year 1928, namely, the spectral examination of the scattered radiations from crystals illuminated by monochromatic light. Valuable information has also come to hand from the study of luminescence spectra and of absorption spectra in the visible and ultraviolet regions at low temperatures. Considerable progress has also been made in the study of infra-red absorption by crystals. By working with thin films, and also by using the highest possible resolving powers, the inherent difficulties and imperfections of infra-red spectroscopy as applied to solids have been minimised. Critical investigations by these diverse methods concur in showing that the vibration spectrum of a crystal held at a sufficiently low temperature as observed in the infra-red region of frequency is effectively *a line spectrum*. From the fact that several procedures of experimental study which are wholly different in principle agree in their indications, it is clear that the spectra of

crystals are inherently of this nature and not by virtue of any particular method of observing them.

The earlier theories of the subject which were based on ideas derived from the behaviour of elastic solids identified the atomic vibrations in a crystal with an immense number of "waves" of diverse wavelengths and frequencies assumed to be present in it. This hypothesis led to a conception of the nature of the vibration spectrum of a crystal radically different from that stated above, viz., that it is a *continuous spectrum*, both in the acoustic and in the infra-red ranges of frequency. That such a view gained currency was perhaps not surprising at a time when experimental knowledge of the spectroscopic behaviour of crystals was of a meagre description. It is, however, altogether inconsistent with the facts known at present as the result of recent research, as will be shown in this paper and the others following it.

The case of diamond which we shall proceed to consider in detail is by far the most suitable test for any theory of the spectroscopic behaviour of crystals. For, it is the solid of the simplest structure and composition of which the vibration spectrum is amenable to theoretical calculation as well as to experimental study. Indeed, all the possible different methods of spectroscopic investigation—five in number—which can be applied to the study of a crystal have been successfully employed in the case of diamond. A further special advantage presented by diamond is that its vibration spectrum appears spread out over a wide range of frequency. This makes it possible with only instruments of moderate power to ascertain and establish the true nature of its spectrum unambiguously, while with the aid of more powerful instruments, it is possible to discover and demonstrate the finest details of its spectral behaviour. A further and notable advantage which arises from the high frequencies of atomic vibration in diamond is that the secondary effects due to thermal agitation are unimportant in its case even at ordinary temperatures. Such effects are markedly present in the majority of crystals and disturb the intrinsic simplicity of their spectra.

2. The eigenvibrations

As is well known, the structure of diamond may be described as consisting of two similar Bravais lattices of carbon atoms of the face-centred cubic type interpenetrating each other. Each atom in one of the lattices is linked to four atoms in the other lattice by valence bonds along the four trigonal axes of symmetry of the crystal. The atoms in the two lattices appear in distinct layers in the octahedral as well as in the cubic planes. In the former set of planes, they are alternately nearer and farther apart, while in the cubic planes they are equidistant. This disposition of the layers is a consequence of the quadrivalence of the carbon atoms and is represented in figure 1, for the octahedral planes and in figure 2 for the cubic ones. A_1 and A_2 represent successive layers of carbon atoms belonging to one lattice,

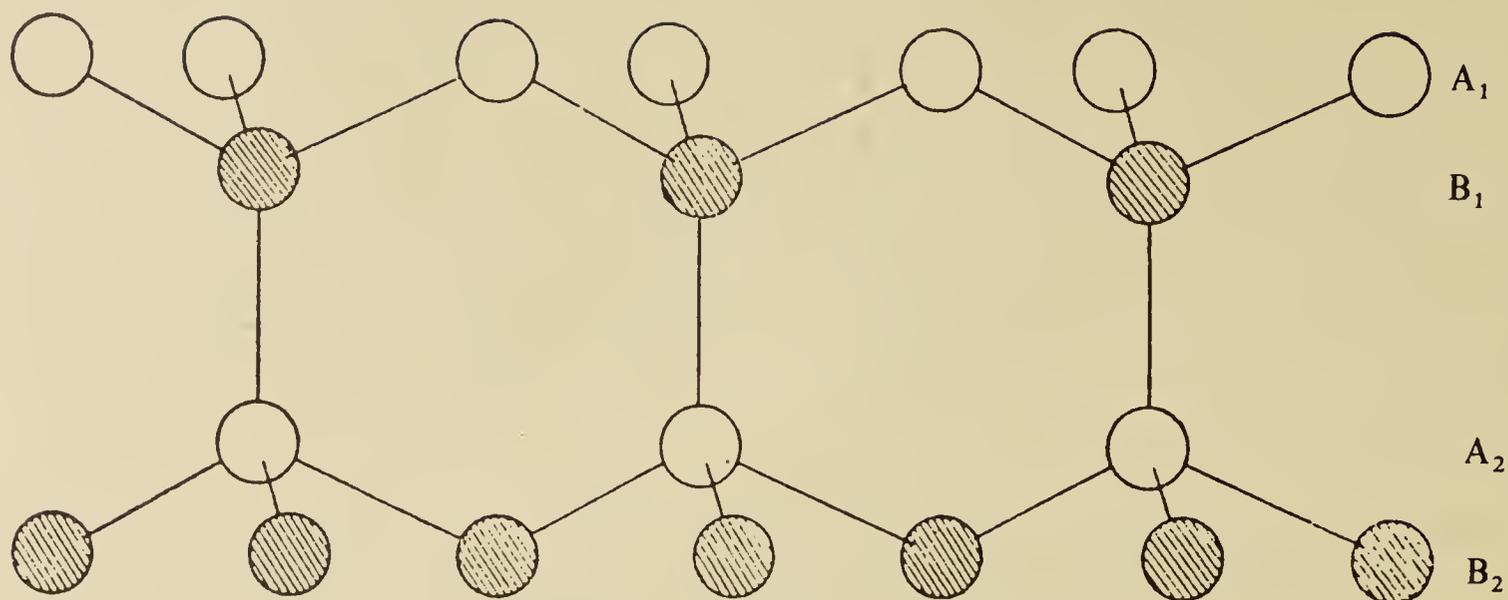


Figure 1. Structure of diamond viewed perpendicular to a trigonal axis.

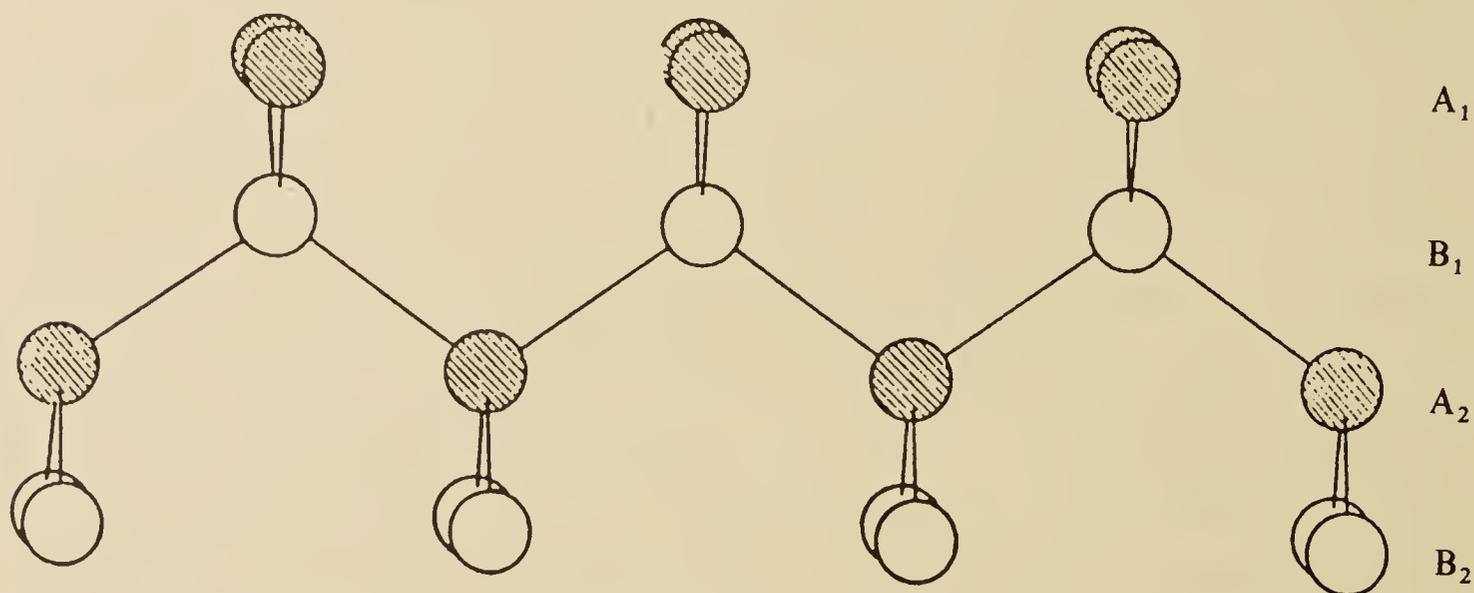


Figure 2. Structure of diamond viewed perpendicular to a cubic axis.

while B_1 and B_2 represent successive layers belonging to the other.

In part I of this series of papers, we have already derived the nine possible eigenvibrations of diamond, and they may be readily visualised with the help of a model of its structure. Figures 1 and 2 above are also helpful in this connection. The principal oscillation of the structure is the one in which the atoms of each lattice move together in the same phase against the atoms in the other lattice moving together in the opposite phase. It is a triply degenerate oscillation, and hence the direction of motion may be either normal or tangential to the atomic planes in either of the two figures, viz., up and down the printed page or horizontally across it. The other eight possible movements arise from the three pairs of possible alternatives; the oscillations may be of the octahedral or of the cubic planes of atoms; the oscillations may be normal or tangential to these planes; the oscillations may be symmetric, or antisymmetric, adjacent layers of the structure belonging to the two lattices moving in the same phase in the symmetric modes, and in opposite phases in the antisymmetric ones. Thus, for

instance, in the tangential symmetric oscillation of the octahedral planes, the layers A_1 and B_1 in figure 1 move together horizontally across the page against the layers A_2 and B_2 moving together in the opposite direction. Similarly, in the tangential antisymmetric oscillation of the cubic planes, the layers A_1 and B_2 in figure 2 move together horizontally across the page against the layers B_1 and A_2 moving together in the opposite direction.

3. The valence forces

The forces coming into play when the atoms in diamond oscillate are principally of two kinds, viz., those due to changes of bond-lengths and those due to changes of bond-angles. The forces of the first kind are predominantly of greater strength, and this fact taken together with the geometry of the modes enables us readily to arrange them in a descending sequence of frequency as shown in table 1. We shall, to begin with, consider only the forces due to the changes of bond-lengths. It is immediately evident that they are absent in the tangential symmetric oscillation of the octahedral planes, as also in the tangential antisymmetric oscillation of the cubic planes described in the preceding paragraph. These two modes have therefore the lowest frequencies and are accordingly placed at the bottom of the table. On the other hand, the tangential antisymmetric oscillation of the octahedral planes, and the tangential symmetric oscillation of the cubic planes both involve large variations of bond-length. By reference to figures 1 and 2, it is seen that the changes of bond-length in each case are exactly the same as in the analogous movements of the two lattices against each other in mode I. Accordingly, these three modes have the highest frequency and are placed at the top of the table. The four modes in which the atomic layers move normally to themselves remain to be considered. It is readily seen that the symmetric and antisymmetric normal vibrations of the cubic planes would have identical frequencies owing to the disposition of the valence bonds and of the atoms in equidistant layers. On the other hand, the symmetric and antisymmetric normal oscillations of the octahedral planes are obviously different. A simple calculation based on the inclination of the valence bonds to the direction of movement shows that the symmetric oscillation would have a higher frequency than the antisymmetrical, while the normal oscillation of the cubic planes would have an intermediate frequency.

In the final ordering of the modes, we have also to consider the forces due to the variations of the bond-angles. These differ notably in the modes VIII and IX in which bond-length variations are totally absent, as also in the modes I, II and III in which they are of equal magnitude, and hence enable us to arrange them in the proper sequence of frequency. The tangential symmetric oscillation of the octahedral planes (mode IX) obviously involves variations of fewer bond-angles than the tangential antisymmetric oscillation of the cubic planes (mode VIII). It

Table 1

Descending order of frequency	Degeneracy	Description of mode
I	3	Oscillation of the two lattices
II	8	Tangential antisymmetric oscillation of the octahedral planes
III	6	Tangential symmetric oscillation of the cubic planes
IV	4	Normal symmetric oscillation of the octahedral planes
V*	3	Normal antisymmetric oscillation of the cubic planes*
VI*	3	Normal symmetric oscillation of the cubic planes*
VII	4	Normal antisymmetric oscillation of the octahedral planes
VIII	6	Tangential antisymmetric oscillation of the cubic planes
IX	8	Tangential symmetric oscillation of the octahedral planes

*Note—Modes V and VI have the same frequency.

therefore now appears at the bottom of the table, with the latter immediately above it. The principal lattice oscillation (mode I) involves variations of all six bond-angles and is therefore placed at the top of the table, followed in order by the tangential antisymmetric oscillation of the octahedral planes (mode II) and the tangential symmetric oscillation of cubic planes (mode III) in which only three bond-angles and one bond-angle respectively vary sensibly. The nine eigenvibrations as thus finally arranged are shown in table 1.

4. Numerical evaluation of the eigenfrequencies

The descending sequence of frequency shown in table 1 is sufficient to enable the modes of vibration manifesting themselves in the spectrum of diamond to be individually identified. It is possible, however, to go further and make a numerical estimate of the frequency of each of the modes, thereby confirming the assignment of the observed spectral frequencies to the different modes and placing their identification on a secure basis. We shall proceed to show how this may be done.

In any eigenvibration, equivalent atoms have the same amplitude of motion, and since the masses of the two sets of equivalent atoms in diamond are the same, it follows that the atomic displacements are also the same. It is sufficient therefore to find the forces acting on any one atom in a given mode of vibration to ascertain

its frequency. The principal forces acting on each atom are (1) the force proportional to its own displacement, and (2) the forces proportional to the displacements of the four atoms with which it is linked by valence bonds. The displacements of the more distant neighbours would also give rise to forces, but these would be smaller, and owing to the alternation of phase in successive layers would tend to cancel each other out. We may accordingly limit ourselves to the forces specified above.

We denote the three force-constants with which we are concerned by P , Q and R . P is the restoring force on the atom under consideration arising from a unit displacement of itself along a cubic axis. Q and R are the forces on the atom arising from a similar displacement of one of the atoms linked with it, Q being parallel to the displacement, and R perpendicular to it. P being taken as a positive quantity, it is evident that Q would be negative and that $P/4$ would be the order of magnitude of its numerical value or rather an upper limit for the same. For, the restoring force P may be regarded as due to the displacement of an atom relatively to its four nearest neighbours, though the more distant atoms may also sensibly contribute. Further, owing to the tetrahedral disposition of the valence bonds, R and Q would be nearly equal to each other. More definitely, it can be said that $Q > R > Q/2$. The upper limit Q for R would be reached if the forces arise solely from the variation of bond-length, but we know that this is not the case and that the variation of bond-angles has also to be considered. The lower limit for R , namely $Q/2$, is set by the consideration that the forces due to variation of bond-angles would then be so large that modes IV, V, VI and VII in table 1 would no longer form a descending sequence of frequency. The ratios $P:Q:R$ are thus known a priori, at least approximately, from considerations based on the structure of diamond.

Denoting the mass of the carbon atom by m , the frequency in wave-numbers by ν and the velocity of light by c , we write

$$4\pi^2\nu^2c^2m = F, \quad (1)$$

where F is the operative force-constant, viz., the magnitude of the force acting on the atom per unit displacement. This is shown for each of the different modes in the second column of table 2. The formulae are readily derived by reference to the modes as described in table 1. We remark that P necessarily appears in each case. Q appears with a factor equal to the number of linked atoms which move in the same phase as the atom under consideration, less the number moving in the opposite phase; the factor is -4 , -2 , 0 , $+2$, 0 , -2 , 0 and $+2$ respectively for the modes as listed. The force-component R is perpendicular to a cubic axis and does not therefore appear in the frequency expressions for modes I, V and VI, the motion being along a cubic axis. In the remaining modes, the movement is along a body-diagonal or a face-diagonal of the cube, and R therefore appears in the formulae with a multiplying factor equal to the number of atoms effective in each case. A check on the formulae is obtained by putting $Q = -P/4$ and $Q = R$, when

Table 2. Calculated and observed eigenfrequencies of diamond

Mode	F (operative force-constant)	$Q = -P/4$ $R = 2Q/3$	$Q = -P/5$ $R = 2Q/3$	$Q = -P/6$ $R = 2Q/3$	Observed frequency
		cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
I	$P - 4Q$	1332	1332	1332	1332
II	$P - 2Q - 2R$	1276	1282	1287	1250
III	$P - 4R$	1216	1230	1240	1232
IV	$P + 2Q - 4R$	1018	1057	1087	1149
V & VI	P	942	993	1031	1088
VII	$P - 2Q + 4R$	860	925	973	1008
VIII	$P + 4R$	544	678	770	752
IX	$P + 2Q + 2R$	385	573	688	620
	$P =$	6.28	6.975	7.536	$\times 10^5$ dynes per cm
	$Q =$	-1.57	-1.395	-1.256	-do-
	$R =$	-1.047	-0.93	-0.837	-do-

the frequency comes out as the same for the first three modes, as zero for the last two and as a descending sequence for those between.

Table 2 makes a comparison of the observed frequencies with those calculated on the basis of the P:Q:R ratios shown at the head of each column, the corresponding numerical values of P, Q and R which give the frequency of the first mode as 1332 cm^{-1} being shown below. It will be seen that there is good agreement between the figures appearing in the last two columns, thus supporting the identification of the modes with the observed spectral frequencies, as well as the theoretical approach on which the calculations are based. The agreement is, of course, not perfect, but this is only to be expected, since the forces have been ignored which arise from the more distant atoms. The fact that Q comes out as $-P/6$ and not as $-P/4$ is a clear indication that such forces are small, but are not negligible. This interpretation of the discrepancies between the figures shown in the last two columns of table 2 is completely confirmed by an investigation of K G Ramanathan (1947) appearing elsewhere in these *Proceedings*. The dynamics of the problem has been very fully worked out by him, taking account of no fewer than 28 atoms in the equations of motion.

5. Activity in light-scattering

We shall now consider the activity of the various modes of vibration in light-scattering. Equivalent atoms in the structure have the same phase in mode I, while they are alternately in opposite phases in successive layers in the other modes. The changes of optical polarisability therefore add up for mode I, while they cancel out (*to a first approximation*) in the other modes. Mode I is therefore active in light-scattering, while the others are not.

Table 3. Theoretical activity of the eigenvibrations
(For explanation see text)

Serial order	Frequency cm ⁻¹	Light scattering		Infra-red absorption	
		1st order	2nd order	1st order*	2nd order
I	1332	Active	Strong	Inactive	Inactive
II	1250	Inactive	Strong	Inactive	Very weak
III	1232	Inactive	Very strong	Inactive	Very weak
IV	1149	Inactive	Strong	Inactive	Weak
V & VI	1088	Inactive	Weak	Inactive	Strong
VII	1008	Inactive	Very weak	Inactive	Strong
VIII	752	Inactive	Inactive	Inactive	Inactive
IX	620	Inactive	Inactive	Inactive	Inactive

**Note*—The entries in the fifth column of the table assume that the electronic structure of diamond has octahedral symmetry. For a discussion of the infra-red activity of the first-order arising when this is not the case, see section 7.

In the second approximation, the non-linear dependence of the optical polarisability on the atomic displacements has to be considered. It is evident that if the *increase* in optical polarisability due to the approach of two atoms is different from the *decrease* due to their recession by an equal amount, the effects of the successive layers would not cancel out completely, leaving a residue which passes through a complete cycle of changes twice during each oscillation and has therefore twice its frequency. Superposition of two modes with different frequencies would, in addition, yield a residual effect with a summational frequency. In considering the magnitude of such effects, it is useful to regard the valence bonds themselves as the units which are optically polarisable. We represent each bond as having an ellipsoid of polarisability of its own. The tetrahedral grouping of the ellipsoids in the crystal secures its optical isotropy in the non-oscillating state. Alterations of bond-lengths during a vibration produce changes in the axial dimensions of the ellipsoids, while variations of bond-angle would alter their orientations. Only major changes could be expected to give observable second-order effects. Accordingly, we are justified in assuming that only changes of bond-length would give such effects. The strength of the effects would be determined principally by the absolute magnitude of the variations of bond-length, and only to a lesser extent by the number of bonds so varying.

The activity of the various eigenvibrations has been assessed and shown in the fourth column of table 3 on the basis of the foregoing considerations. Modes VIII and IX do not involve changes of bond-length and should therefore be inactive. Mode VII is a normal oscillation of the octahedral layers involving changes of three bond-lengths out of every four, but these changes are very small. Accordingly, this mode should exhibit only a very weak second-order activity. Modes V and VI are normal oscillations of the cubic planes in which two out of

every four bonds vary in length, but the changes are definitely larger than in mode VII. Their activity should therefore be greater than that of mode VII. In mode IV, only one bond out of every four varies, but the entire motion is along this bond, and the change in its length is therefore considerable. Accordingly, this mode should be strongly active. In the three remaining modes of highest frequency in the table, the bond-length variations are large, but the number of bonds varying is different, being four in mode I, three in mode II, and two in mode III. The *individual* variations in bond-length are greatest in mode III, less in mode II and least in mode I. Accordingly the second-order activity in light-scattering should be strongest in mode III, less in mode II, and least in mode I, though very considerable in all three cases.

The second-order activity is essentially dependent on the absolute magnitude of the atomic displacements and unless these are large, their results would be of negligible intensity. The atomic displacements are determined by the consideration that the energy of vibration is $h\nu$ for a single excitation and $2h\nu$ for a double excitation. The amplitudes of vibration would be very small and the second-order effects, therefore wholly unobservable if this energy be distributed over the entire volume of the crystal or even over a large number of lattice cells. We may remark further, that since the *elastic vibrations* of a crystal extend over its whole volume, they cannot exhibit any second-order activity in light-scattering. The first order activity is also cancelled out completely by optical interference except in the very special case of a coherent reflection.

6. Activity in infra-red absorption

To simplify the discussion of the activity of the modes in infra-red absorption, we shall here restrict ourselves to the case in which the electronic structure of diamond can be assumed to possess octahedral symmetry. The distribution of electron density has then a centre of symmetry at the point midway between every pair of linked carbon atoms. Since, further, the carbon atoms have equal masses, these points would continue to be centres of symmetry of the electron distribution in mode I, which would therefore be inactive to all orders of approximation. The remaining modes (II to IX) would also be inactive but for a different reason, viz., that the phase of the vibration is reversed at each successive layer of atoms and the effects of successive layers would therefore cancel each other out in *the first approximation*.

We have now to consider whether the oscillations of the atomic layers in the modes II to IX would give rise to electric moments in the individual layers large enough to give an *observable second-order effect of double frequency*. The tetrahedral symmetry of diamond ensures that the atomic nuclei are also the centres of distribution of the negative electric charges surrounding them. But when the layers of atoms oscillate *normally* to themselves and the neighbours on

either side of each layer do not move *symmetrically* with respect to it, the tetrahedral symmetry of distribution of charge would evidently be disturbed. As a result, each atomic plane would become an oscillating electric double layer, thereby giving rise to an observable second-order infra-red activity. A *tangential* oscillation of the atomic layers would, however, not be effective in the same manner or to the same extent. If, further, as in modes VIII and IX, the valence bonds only tilt but do not stretch, no appreciable dipole moments could develop. The relative activities of the various modes can be assessed on the basis of these considerations and are shown in the last column of table 3. We may remark that modes V and VI are normal oscillations of the cubic planes, while modes IV and VII are those of the octahedral planes. In mode VII, the closely adjacent atomic layers approach and recede from each other, while the more distant ones remain at the same distance. In mode IV, the situation is reversed, viz., the closely adjacent layers remain at the same distance apart from each other, while the more distant one recedes and approaches. In these circumstances, it is clear that mode VII should exhibit greater infra-red activity than mode IV, as shown in the table.

7. The spectroscopic facts

The spectroscopic behaviour of diamond has been very thoroughly investigated at Bangalore with the result that we have a wealth of experimental results at our disposal. The data for the spectral frequencies obtained by different methods have been set together in parallel columns and represented in the form of a chart (figure 3). For lack of space, the chart omits reference to the infra-red *emission* spectra. These, however, closely follow the corresponding *absorption* spectra.

The scattering of light—Spectroscopic studies made prior to 1943 had revealed that diamond exhibits in light-scattering a frequency shift of 1332 cm^{-1} , evidently representing our mode I. Following on the publication of his theory (Raman 1943), the present writer confidently ventured to predict that diamond should also exhibit a second-order spectrum with other frequency shifts explicable as octaves and combinations of its eight fundamental frequencies. An experimental investigation undertaken by Dr R S Krishnan soon afterwards confirmed this prediction. A detailed report on his latest findings appears in a paper by Dr R S Krishnan (1947) appearing in these *Proceedings*. His earlier papers (1944, 1946) on the subject also contain valuable experimental material to which the reader is referred. It will suffice here to remark that these publications clearly establish the discrete character of the vibration spectrum of diamond indicated by the present theory. *Of particular significance is the notable intensity of the second-order spectrum in relation to that of the first-order, which clearly demonstrates that the energy of the high-frequency vibrations in the crystal is not diffused through it in the*

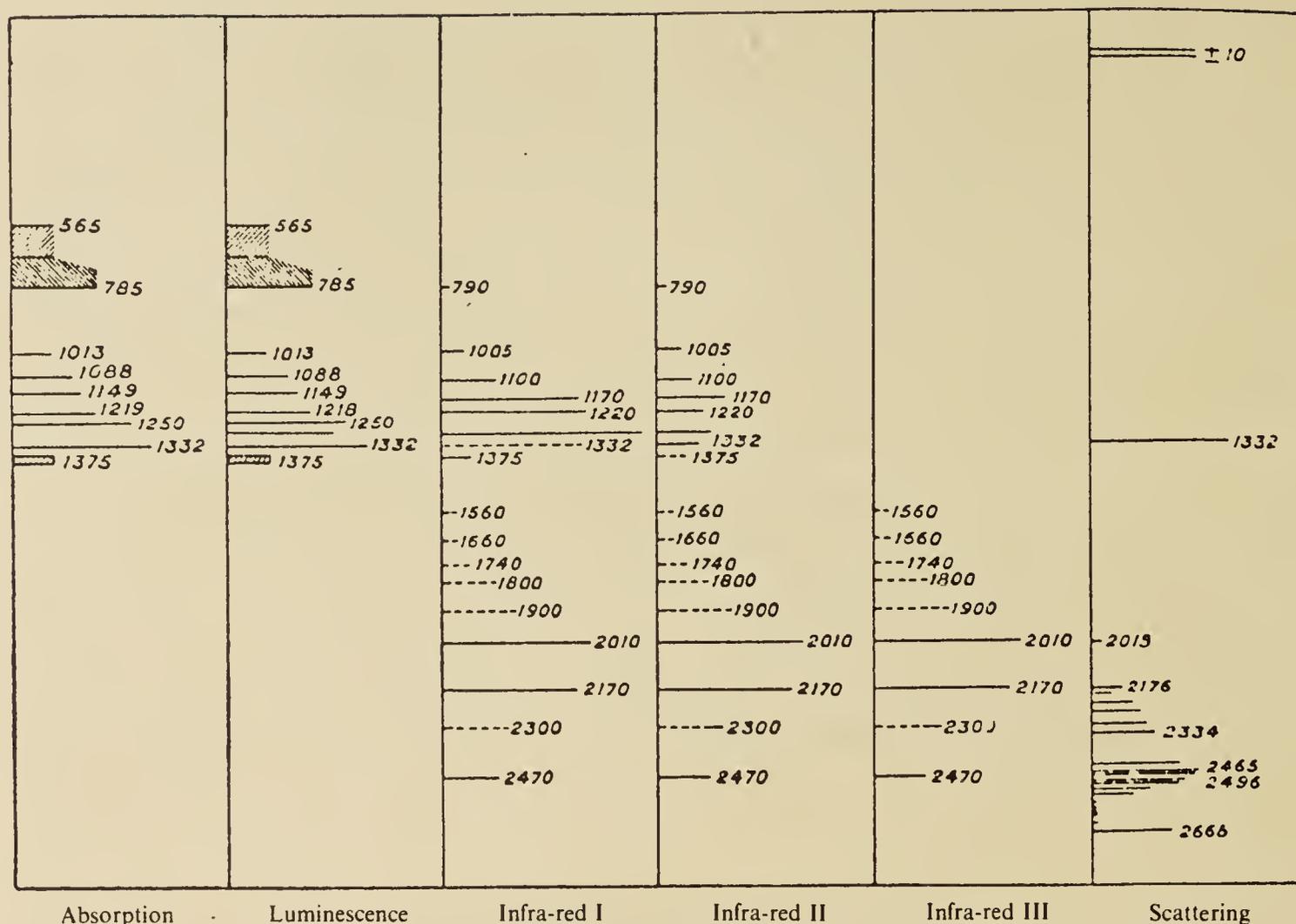


Figure 3. Spectral frequencies in cm^{-1} as observed by various methods.

form of a "wave", but is concentrated in extremely small regions comparable in volume with its lattice cells. The interesting fact that the octave of the 1332 line is not the most intense one in the second-order spectrum – being, in fact – the third in order of intensity – finds its explanation in the theoretical considerations set out in section 5 of the present paper. Dr R S Krishnan's earlier spectrograms did not reveal the octave of mode VII. The theoretical prediction that it should appear in the second-order spectrum though only with a very small intensity has, however, been confirmed in his most recent investigations.

Infra-red absorption—All diamonds without exception exhibit an infra-red absorption in the region of frequencies between 1560 cm^{-1} and 2470 cm^{-1} , the strength of which shows no appreciable variation from specimen to specimen. It is therefore clearly a fundamental property of diamond. The existence of such absorption and its spectral characters are explained by the theoretical considerations set out in section 6 of the present paper. The two prominent peaks in infra-red absorption appearing at 2010 cm^{-1} and 2170 cm^{-1} are clearly the octaves of the fundamental frequencies 1008 and 1088.

A study of the crystal forms of diamond from a new point of view (Raman and Ramaseshan 1946) has shown clearly that the crystal symmetry of diamond is, in general, only tetrahedral, though some diamonds undoubtedly possess the higher or octahedral symmetry of structure. The fact that the great majority of diamonds

exhibit infra-red activity of the first order ceases to be surprising in the light of this finding. The striking variations in the strength of such activity in different specimens also find their natural explanation in the interpenetration of the positive and negative tetrahedral structures which is also clearly indicated by the crystallographic evidence. From our present point of view, these facts are chiefly interesting since infra-red activity of the first-order makes the fundamental frequencies themselves accessible to observation. The three columns marked (I), (II), (III) in figure 3 represent results typical of those observed with different diamonds.

A full report on the infra-red absorption spectra of numerous diamonds is made by K G Ramanathan (1947) in a paper appearing in these *Proceedings*. It will suffice here to make a few remarks supplementing those contained in section 6 of the present paper on the theoretical aspects of the subject. The small difference in structure which gives rise to the first-order activity in most diamonds would not make any difference in respect of the second-order activity. Hence no changes are necessary in respect of the entries in the last column of our table 3. If there were no interactions between the different normal modes, tetrahedral symmetry would result in making mode I active, the other modes remaining inactive in the first approximation. Actually, however, the differences between mode I and the other modes are due only to the differences in the phases of movement of the atomic layers. In view of this geometric similarity of the movements and the anharmonicity of the forces arising from the atomic displacements, a strong interaction between the different "normal" vibrations is inevitable. Such interaction would be the more powerful, the smaller the difference of frequency between mode I and the other mode under consideration. We need not therefore be surprised to find, as is actually the case, that the infra-red activity of mode I results in the modes with frequencies not very remote from it also showing an observable activity of the first-order.

Emission and absorption by luminescent diamonds—The emission spectra of luminescent diamonds are of two different kinds, viz., "blue luminescence" and "yellow luminescence", and there are also two corresponding types of absorption spectra. These have their origin in electronic transitions which appear at λ 4152 and λ 5032 respectively and combine with vibrational transitions in the crystal, giving a spectrum stretching respectively towards longer wavelengths in emission and towards shorter wavelengths in absorption. The spectra are best studied with the diamond held at liquid air temperatures, the features observed in the spectra being then most sharply defined. The vibrational frequencies as determined from the emission and absorption spectra are practically identical. Indeed, these spectra exhibit a remarkable mirror-image symmetry about the electronic transition (λ 4152 or λ 5032 as the case may be), in respect of both position and distribution of intensity, thereby affording a clear demonstration that they arise from the combination of the electronic and vibrational frequencies of the crystal.

The spectroscopic behaviour of no fewer than 28 diamonds in luminescence and absorption has been investigated in detail by Miss Anna Mani (1944). Her paper may be consulted for a full report on the subject including further details. One of her most interesting findings is that the vibration spectra accompanying the λ 4152 and λ 5032 electronic transitions are strikingly different in respect of the distribution of intensity. The vibrational transitions accompanying the λ 4152 transition are principally those lying in the upper or infra-red range of frequency and their overtones, while those accompanying the λ 5032 electronic transitions are principally the "elastic" vibrations of lower frequency. Hence, the "blue" luminescence and the corresponding absorption spectra are those which are important from our present point of view. Miss Mani has shown that the λ 4152 transition is really a doublet, the width of the components as well as their separation varying with the specimen under study. Even at liquid air temperature, the total width covered by the electronic transition is never less than 20 cm^{-1} and may be as such as 50 cm^{-1} . This width necessarily appears in the spectra when the electronic frequency combines with the vibrational frequencies and hence obscures to some extent the monochromatic character of the latter. Even so, the discrete nature of the vibrational spectrum in the upper ranges of frequency is clearly manifest in the emission and absorption by "blue" luminescent diamonds when held at liquid air temperatures. The observed frequency differences are shown in our chart (figure 3).

8. Summary

Considerations based on the crystal structure of diamond enable its nine eigenvibrations to be arranged on a descending scale of frequency. The magnitude of the force-constants involved can also be defined within narrow limits. The numerical values of the frequencies evaluated on the basis of the theoretical formulae show a close agreement with the observed values. The geometry of the modes determines the changes in bond-polarisabilities and electron distributions produced by them, from which their activities in light-scattering and in infra-red absorption can be ascertained both in the first and in the second approximation. A comparison of the results with the experimental facts shows a striking agreement. The observed intensity of the second-order effects in relation to those of the first order indicates that the eigenvibrations are localised in volume elements comparable in size with the lattice cells of the crystal.

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The vibration spectra of crystals—Part III. Rocksalt

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2. The nature of the interatomic forces
3. The eigenvibrations
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8. Summary

1. Introduction

Rocksalt is typical of the so-called ionic crystals and is a much-discussed substance. The evaluation of its characteristic vibration frequencies on the basis of the theory set out in part I, and the consideration of its spectroscopic behaviour in the light of that theory will form the subject of the present paper. From an experimental point of view, the case of rocksalt is a less favourable one than that of diamond, the frequencies being very low and hence crowded together into a region of the spectrum where observation is difficult and the available resolving powers are small. Nevertheless, as we shall see, the main facts have been quite clearly established and are in striking accord with the theoretical deductions.

2. Nature of the interatomic forces

Discussions of the energy of formation of the alkali halides and of their physical properties usually proceed on the basis that the main interaction between the constituent particles in these crystals is the ordinary electrostatic or the Coulomb

force between the ions, and that these forces which tend to contract the dimensions of the crystal are balanced by repulsive forces which vary much more rapidly with interatomic distance than do Coulomb forces between charges. Various additional interactions, e.g., Van der Waals forces, have also been considered by way of refinement of the theory. That the electrostatic or the Madelung term is the largest in the expression for the cohesive energy of the alkali halides thus derived might lead one to believe that the electrostatic forces would also principally determine the frequencies of vibration of the ions about their positions of equilibrium. Actually, however, this is not the case, as may readily be shown by considering the consequences of the cubic symmetry of the ordering of the ions in the crystal.

Since the electrostatic forces acting on the ions vanish when they are located at the points of the lattice, it follows that at these points $(\partial V/\partial x) = (\partial V/\partial y) = (\partial V/\partial z) = 0$, where V represents the electrostatic potential in the vicinity of a lattice point due to all the ions except the one which is situated at that point. The cubic symmetry of the ordering also demands that $(\partial^2 V/\partial x^2) = (\partial^2 V/\partial y^2) = (\partial^2 V/\partial z^2)$. Combining these relations with Laplace's theorem which states that the sum of these three quantities is zero, it follows that each of them would be individually zero. In other words, not only does the electrostatic field at a lattice point due to the surrounding ions vanish, but it also vanishes in its immediate vicinity. If, therefore, one of the ions is displaced a little from its position of equilibrium, the surrounding ions being undisturbed, there would be no force tending to restore the displaced ion to its position of equilibrium. The same situation would arise if we imagine all the Na^+ ions to be displaced a little in one direction and all the Cl^- ions to be displaced a little in the opposite direction, so that each set of ions retains its cubic symmetry of arrangement. The resultant electrostatic force on each Na^+ ion and on each Cl^- ion in their displaced positions would vanish, and the frequency of the resulting oscillation would be zero, if forces of other descriptions were non-existent. We are accordingly compelled to recognize that the frequency of the vibration would be determined entirely by interatomic forces which are not primarily of electrostatic origin. It follows that these are essentially short-range forces which have a considerable magnitude as between neighbouring atoms but diminish very quickly as between more distant ones.

3. The eigenvibrations

As in the case of diamond discussed in the preceding paper, the rocksalt structure has nine eigenvibrations, eight of which may be described as normal or tangential oscillations of the octahedral or cubic layers of ions *alternately in opposite phases*, and the ninth as an oscillation with respect to each other of the two interpenetrating lattices of Na^+ and Cl^- ions respectively. These modes may be readily visualised with the aid of diagram of the structure of rocksalt (figure 1). As

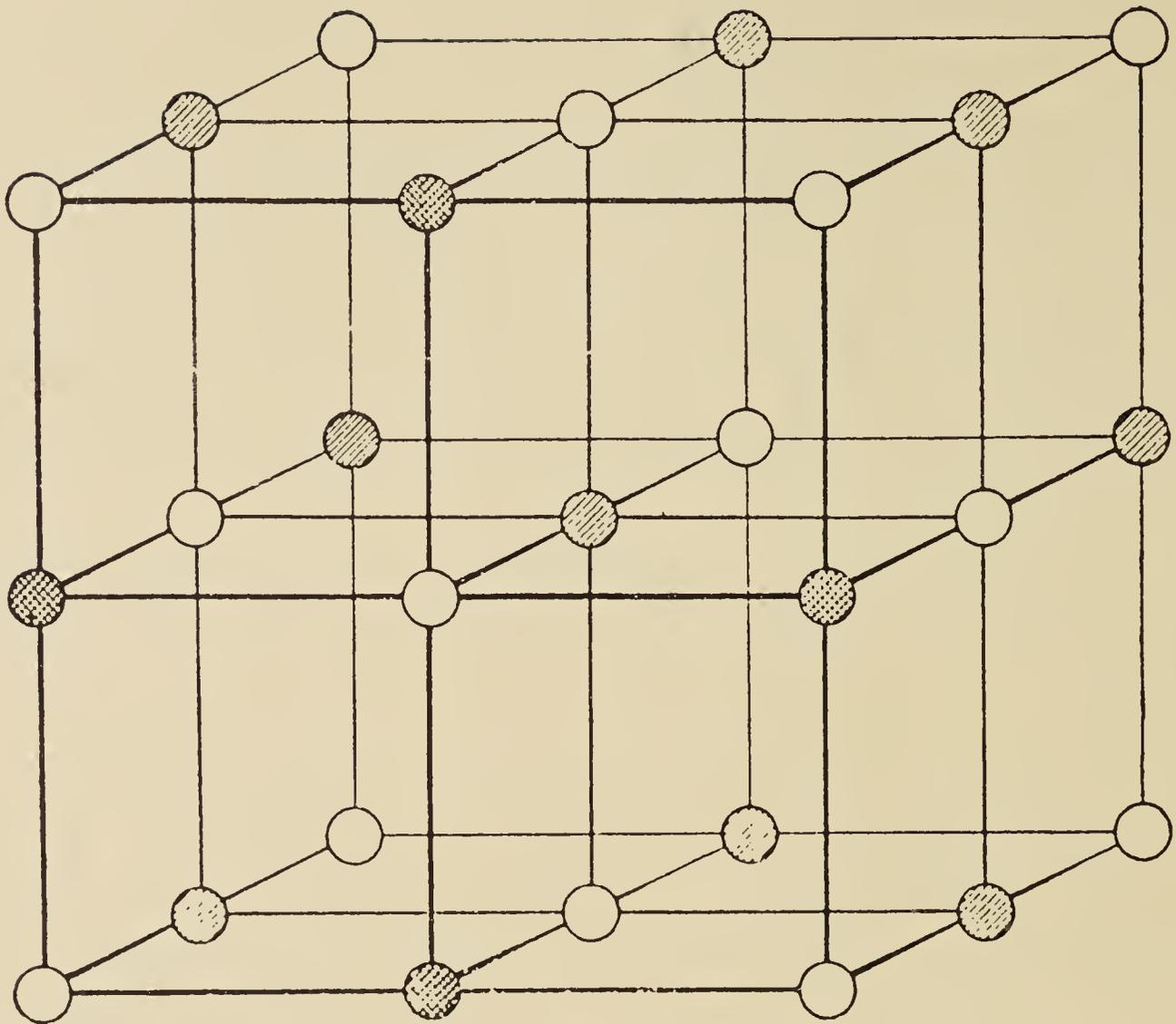


Figure 1. The structure of rocksalt.

in the case of diamond again, the first step we shall take is to arrange these nine eigenvibrations in a descending sequence of frequency, thereby facilitating a comparison of the theoretically derived spectrum with the experimental data. Such arrangement is readily possible in view of the conclusion stated earlier, viz., that the atomic interactions which determine the vibration frequencies are short-range forces.

We may, in the first instance, consider the interactions between each Na^+ ion and the 6 surrounding Cl^- ions and similarly also the interaction between each Cl^- ion and the six surrounding Na^+ ions, *neglecting the forces due to the more distant ions in each case*. So long as the octahedral grouping of the surrounding ions is undisturbed, the restoring force per unit displacement acting on the central ion when it is displaced would be independent of direction, and it is also evident that it would be the same whether it is Na^+ or Cl^- . We shall denote this force by P and assume that it arises from an approach or recession of the Na^+ and Cl^- ions relatively to each other. The frequency of an oscillation would accordingly be determined by the magnitude of such displacements and by the masses of the moving particles. On this basis, the nine eigenvibrations fall into four groups, consisting of 3, 2, 2 and 2 respectively, each group having the same frequency. The first group of 3 eigenvibrations consists of:

- (I) The *normal* oscillation of the cubic planes with Na^+ and Cl^- ions in these planes moving *in the same phase*;
 (II) the *tangential* oscillation of the cubic planes, with the Na^+ and Cl^- ions in these planes moving in *opposite phases*; and
 (III) the oscillation of the Na^+ and Cl^- lattices against each other *in any arbitrary direction*.

It can be seen from figure 1 that the displacements of the Na^+ and Cl^- ions relatively to each other are the same in all these three cases. Accordingly, the operative force-constant is equal to P and the frequency ν of vibration in wave-numbers is given by the formula

$$4\pi^2\nu^2c^2 = P\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \quad (1)$$

m_1 and m_2 being masses of the Na^+ and Cl^- ions respectively. The second group of eigenvibrations consists of:

- (IV) the normal oscillations of the Na^+ ions in the octahedral planes, the Cl^- ions remaining at rest; and
 (V) the tangential oscillations of the Na^+ ions in the octahedral planes, the Cl^- ions remaining at rest. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = P \cdot \frac{1}{m_1} \quad (2)$$

The third group of eigenvibrations consists of:

- (VI) the normal oscillations of the Cl^- ions in the octahedral planes, the Na^+ ions remaining at rest; and
 (VII) the tangential oscillations of the Cl^- ions in the octahedral planes, the Na^+ ions remaining at rest. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = P \cdot \frac{1}{m_2} \quad (3)$$

The fourth group of eigenvibrations consists of:

- (VIII) the normal oscillations of the cubic planes of atoms, the Na^+ and Cl^- ions in these planes moving *in opposite phases* and
 (IX) the tangential oscillations of the cubic planes of atoms, the Na^+ and Cl^- ions in these planes moving *in the same phases*. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = 0. \quad (4)$$

For a final ordering of the nine eigenvibrations in a descending sequence of frequency, we have to consider also the forces of interaction between each Na^+

ions and the 12 surrounding Na^+ ions, and similarly also the forces between each Cl^- ion and the 12 surrounding Cl^- ions. It is readily seen that mode I would then have the highest frequency in the first group, since 8 out of the 12 like ions move in the opposite direction to the ion under consideration and thereby increase the restoring force. In mode II, 4 of the like ions move in the same direction and 4 in the opposite direction, cancelling out each other's effects. In mode III, all the 8 like ions which exert appreciable forces move in the same direction, thus diminishing the restoring force and therefore also the vibration frequency. The 3 modes thus arrange themselves in the order indicated. In the second and third groups it is readily seen from considerations similar to those stated above, that the normal modes would have higher frequencies than the tangential ones. This is also the case in the fourth group, the frequencies of which no longer vanish when the forces between like ions are taken into consideration. These have naturally the lowest frequencies of all the nine eigenvibrations. Table 1 summarises the foregoing results.

Table 1. Eigenvibrations of the rocksalt structure

Descending sequence of frequency	Degeneracy	Oscillating units	Direction of motion	Detailed description
I	3	Cubic planes	Normal	Na and Cl ions moving in the same phase
II	6	Cubic planes	Tangential	Na and Cl ions moving in opposite phases
III	3	Two lattices	Arbitrary	Na and Cl ions moving in opposite phases
IV	4	Octahedral planes	Normal	Na ions moving and Cl ions at rest
V	8	Octahedral planes	Tangential	Na ions moving and Cl ions at rest
VI	4	Octahedral planes	Normal	Cl ions moving and Na ions at rest
VII	8	Octahedral planes	Tangential	Cl ions moving and Na ions at rest
VIII	3	Cubic planes	Normal	Na and Cl ions in opposite phases
IX	6	Cubic planes	Tangential	Na and Cl ions in same phases

4. Evaluation of the eigenfrequencies

To carry the matter a step further and evaluate the frequencies of each of the nine eigenvibrations, we shall make use of the exact theoretical formulae derived by

K G Ramanathan (1947) in a paper appearing in these *Proceedings* which take into account the interaction between the ions of each kind and their 26 nearest neighbours. They contain 11 independent constants which express the forces arising from such interactions and are connected by two additional relations. Ramanathan's formulae may be simplified by ignoring the effect of the 8 most

Table 2. Frequency expressions
(P and P' are positive; T and T' are negative.)

Descending sequence of frequency	$4n^2v^2c^2$	Description of mode
I	$\frac{P - 8T}{m_1} + \frac{P' - 8T'}{m_2} + \frac{16(T + T')}{m_1 + m_2}$	Normal oscillation of cubic planes with Na and Cl in same phase
II	$\frac{P}{m_1} + \frac{P'}{m_2} + \frac{8(T + T')}{m_1 + m_2}$	Tangential oscillation of cubic planes with Na and Cl in opposite phases
III	$\frac{P + 8T}{m_1} + \frac{P' + 8T'}{m_2}$	Oscillation of the two lattices in opposite phases
IV	$\frac{P - 8T}{m_1}$	Normal oscillation of Na ions in octahedral planes
V	$\frac{P + 4T}{m_1}$	Tangential oscillation of Na ions in octahedral planes
VI	$\frac{P' - 8T'}{m_2}$	Normal oscillation of Cl ions in octahedral planes
VII	$\frac{P' + 4T'}{m_2}$	Tangential oscillation of Cl ions in octahedral planes
VIII	$\frac{16(T + T')}{m_1 + m_2}$	Normal oscillation of cubic planes with Na and Cl in opposite phases
IX	$\frac{8(T + T')}{m_1 + m_2}$	Tangential oscillation of cubic planes with Na and Cl in same phase

remote ions expressed by his constant V appearing in them, and also by putting his constants R , S and S' all equal to zero. The former step is justified on the view that we are here concerned with short-range forces, and the latter by the consideration that the constants R , S and S' refer to forces which arise from displacements which do not alter the distance between the interacting ions. On any reasonable view of the origin of the interactions in an ionic crystal with cubic symmetry, such forces should be vanishingly small in comparison with the forces arising from displacements which alter the distances between the interacting ions. It may be remarked also that T and U in Ramanathan's formulae represent forces between two ions of the same kind arising from a unit displacement of one of them, the force T being parallel to the displacement and the force U transverse to it, both being inclined at the same angle of 45° to the line joining the two interacting ions. In these circumstances and considering the ionic nature of the structure, it is a justifiable simplification of the formulae to put $T = U$ and similarly also $T' = U'$. With these simplifications, the final formulae contain only four unknown constants P , P' , T , T' which are connected by the relation

$$(P + 8T) = (P' + 8T'). \quad (5)$$

Further,

$$P \gg T \quad \text{and} \quad P' \gg T' \quad (6)$$

from which it follows

$$P \approx P'. \quad (7)$$

The formulae for the frequency of the nine eigenvibrations as thus simplified are listed in table 2.

One of the noteworthy features which emerge from the table is that the vibration in which the two lattices move in opposite phases is not that of the highest frequency but is only the third in the list, though the frequency differences between it and the two others above are not large. The four modes appearing in the middle of the table fall into pairs whose frequencies are approximately as the square roots of the masses of the chlorine and the sodium ions. The two modes at the foot of the table stand out from the rest by reason of the fact that their frequencies depend only on the weak interactions between similar ions instead of on the stronger interactions between the dissimilar ones, as in the case of the other modes. It will be noticed that the ratio of their frequencies is $\sqrt{2}$.

5. Activity in light-scattering

The eight eigenvibrations which are movements of the cubic and octahedral layers of atoms in the crystal are necessarily inactive in light-scattering *in the first*

approximation, since the motion is in opposite phases in alternate layers. The oscillation of the lattices of Na and Cl ions with respect to each other is also inactive but for a different reason, namely the location of the Na and Cl ions alternately along the cube axes, in consequence of which the variations of their optical polarisability resulting from their movements cancel out *in the first approximation*.

In the second approximation, all the nine modes may be active, giving rise to octaves and combinations of the fundamental frequencies as shifts in light-scattering. The intensity of the observable effects would however depend notably on various factors, including especially the nature of the movements of the neighbouring Na and Cl ions with respect to each other. These movements are very similar in modes I, II and III, the two Cl^- ions on each side of a Na^+ ion along the cube axis respectively approaching and receding from it, while the two Na^+ ions on each side of a Cl^- ion behave similarly with respect to the latter. *Provided the amplitude of atomic movements is sufficiently large*, which would be the case in the present theory which regards the movements as restricted to extremely small volume elements in the crystal, each pair of neighbouring Na^+ and Cl^- ions at the phase of their nearest approach would have a polarisability greater than the value averaged over the whole period, thus giving rise to a variation of double frequency. Modes I, II and III would therefore all be active to much the same extent, but since mode II has a degeneracy 6, it should appear as the octave more strongly than either mode I or III which has a degeneracy of 3 only.

We may now consider modes IV and V which represent oscillations of the Na^+ ions only lying in the octahedral layers, as also modes VI and VII which represent similar oscillations of the Cl^- ions only. We notice that the nature of the approach of the Na^+ and Cl^- ions to each other is very different in the normal and tangential modes in each case. In the normal modes, viz., IV and VI, six ions of one kind simultaneously approach or recede from an ion of the other kind, while in the tangential modes, viz., V and VII, two ions of one kind approach, two recede, and two others remain at the same distance. Hence the changes of polarisability should be much larger in the normal modes IV and VI than in the tangential modes V and VII. Further, since the refractivity of the Cl^- ion is very much larger than that of Na^+ , it follows that mode VI in which the six Cl^- ions surrounding a Na^+ ion simultaneously approach or recede from it should display a much stronger activity in light-scattering than mode IV in which six Na^+ ions simultaneously approach or recede from a Cl^- ion. Indeed, one may justifiably infer that in respect of intensity in second-order scattering, mode VI would transcend in intensity all the other eight modes. Mode VIII which is a normal oscillation of the cubic planes involves only small changes in the relative distance of the Na^+ and Cl^- ions and should therefore be very weak in light scattering, while mode IX which is transverse oscillation of the same planes should be still weaker.

6. Activity in infra-red absorption

Since the two interpenetrating lattices in the structure of rocksalt consist of dissimilar particles, their oscillation against each other (mode III in our table) is necessarily active in infra-red absorption. In all the other eight eigenvibrations, the phase of the motion is reversed at each successive layer, and hence *if regarded as independent normal vibrations of the structure*, they should be inactive in respect of infra-red absorption. The assumed independence of the modes in respect of their excitation by infalling radiation is, however, very far from corresponding with reality. Owing to the anharmonicity and the finite amplitudes of oscillation, the different eigenvibrations are in effect coupled with each other, and hence any one mode which is active would induce an activity in the other so-called inactive modes. Modes I and II are very similar to mode III in their general character, since the latter may be regarded as being either a normal or a tangential oscillation of the layers of the Na^+ and Cl^- ions in the crystal parallel to the cubic planes. They also differ from it comparatively little in frequency. Hence the intense activity of mode III, consequential on the Na^+ and Cl^- ions carrying opposite charges of electricity, must necessarily also result in inducing a strong activity of modes I and II. Mode III may likewise be regarded as a normal or tangential oscillation of the octahedral layers of the Na^+ and Cl^- ions in the crystal against each other. Hence the intense activity of mode III would similarly induce an activity of modes IV, V, VI and VII, but in a much less measure than in the case of modes I and II, since the former involve only the Na^+ or the Cl^- layers moving but not both, and also since the approximation in frequency is much less close. We may therefore conclude that the first-order infra-red activity of rocksalt would be very strong for modes I, II and III, and would fall off rapidly as we pass successively to modes IV, V, VI and VII. Modes VIII and IX could scarcely be expected to show any such induced activity of the first order in view of their very low frequencies.

Second-order infra-red activity may arise either from mechanical or electrical anharmonicity. In the present case, since the Na^+ and Cl^- ions carry electric charges, it is the mechanical anharmonicity with which we are principally concerned. Since mode III has an intense first-order activity, it should also be active in the second order. The other eight modes being inactive in the first order if regarded as independent normal vibrations, they can be active in the second order only by reason of electrical anharmonicity. Such activity would however be much less important in the circumstances of the case than the activity induced by their proximity in frequency to the intensely active fundamental vibration, viz., mode III. In other words, such of the octaves and combinations of the various primary frequencies as are not too remote from the fundamental frequency of mode III may be expected to become active to an extent determined principally by such contiguity.

7. The spectroscopic facts

The results set out in the four preceding sections taken as a whole give us a theoretical picture of the spectroscopic behaviour of rocksalt capable of being compared with the picture of the actual facts as observed by various investigators. Such a comparison shows a striking agreement, both generally and in details, and thus confirms the correctness of the theoretical approach made to the problem. For the sake of convenience, we shall make the comparison in three successive steps.

The frequency spectrum—Table 2 gives the theoretical formulae for the frequencies in terms of four force-constants, viz., P , P' , T and T' . These constants are not all independent but are connected with each other by the relation $(P + 8T) = (P' + 8T')$, with the further indication that P and P' are nearly equal to each other, and that both are very much larger than T and T' . We can make use of these relationships to simplify the formulae still further by replacing both P and P' in the expressions by a single constant P which is the mean of the two, and similarly replacing T and T' by a single constant T which is their mean. From the structure of the formulae, it is evident that such replacement would not materially alter the numerical value of any of the frequencies, while on the other hand, it affords the advantage of enabling us to express all the nine frequencies in terms of two independent constants only, one of which is very much larger than the other. Table 3 shows the formulae as thus simplified in the second column, μ being the usual symbol for the reduced mass of the Na^+ and Cl^- ions. With the assumed values of P and T shown at the head of the table, the numerical values have been calculated and shown in the third column in wave-numbers. The fourth column shows the observed frequencies, derived from the investigation by Dr R S Krishnan on the second-order spectrum of light-scattering reported in these *Proceedings* (1947). It will be noticed that there is excellent agreement throughout.

Activity on light-scattering—In his paper on the case of rocksalt appearing in these *Proceedings*, Dr R S Krishnan (1947) has set out and discussed the facts ascertained by him in full detail, and it is scarcely necessary therefore to traverse the same ground here. It is sufficient to remark that in all respects, viz., the discrete structure of the spectrum, the magnitude of the frequency shifts and the relative intensities with which they appear, the experimental facts are in agreement with the indications of theory set out in section 5 above. Of particular significance is the observation made by Krishnan that the sharp and intense line with a frequency shift of 235 cm^{-1} , which is a conspicuous feature in the spectrum as recorded even with small instruments, remains sharp and gains in intensity relatively to the rest of the spectrum when recorded with instruments of higher

Table 3. Calculated and observed values of the eigenfrequencies
($P = 2.422 \times 10^4$ dynes per cm. $T = -0.053 \times 10^4$ dynes per cm.)

Serial order	$4\pi^2\nu^2c^2$	Calculated frequency cm^{-1}	Observed frequency cm^{-1}	Activity in light-scattering
I	$\frac{P - 8T}{\mu} + \frac{32T}{m_1 + m_2}$	172	175	Strong
II	$\frac{P}{\mu} + \frac{16T}{m_1 + m_2}$	164	167	Very strong
III	$\frac{P + 8T}{\mu}$	157	150	Strong
IV	$\frac{P - 8T}{m_1}$	145	143	Strong
V	$\frac{P + 4T}{m_1}$	128	129	Weak
VI	$\frac{P - 8T}{m_2}$	117	117	Very strong
VII	$\frac{P + 4T}{m_2}$	103	101	Weak
VIII	$\frac{32T}{m_1 + m_2}$	70	67	Very weak
IX	$\frac{16T}{m_1 + m_2}$	50	43	Very weak

dispersion and greater resolving power, thereby clearly demonstrating its monochromatic character. As will be seen from table 3, this line represents the octave of mode VI. It appears with an intensity transcending that of all other features in the spectrum, a fact which is readily understood since in this mode, the Cl^- ions which have a far higher refractivity than the Na^+ ions simultaneously approach towards or recede away from the latter in groups of six at a time.

Activity in infra-red absorption—The fundamental mode of highest frequency and its overtones sharply define the upper limits of frequency of the successive orders of spectra. Expressed in wavelengths, these limits are respectively 57μ , 29μ , 19μ and 14μ . On our present theory, we should expect large changes in the behaviour of rocksalt on passing over these limits. In agreement with this expectation, the observational data show a transition from nearly perfect transparency to

practically complete opacity for a thickness of 5 cm in the wavelength range from $14\ \mu$ to $19\ \mu$. A similar transition occurs for a thickness of 0.05 cm in the wavelength range of $19\ \mu$ to $29\ \mu$, and for a thickness of 0.0005 cm in the wavelength range from $29\ \mu$ to $57\ \mu$. For the last mentioned thickness the most intense absorption is found in the region from $57\ \mu$ to $66\ \mu$ which includes the frequencies of the three most strongly active modes I, II and III. The overall picture of the observed behaviour of rocksalt is thus in accord with the indications of the theory.

In view of the numerous overtones and combinations present and also considering the prominent role played by mechanical anharmonicity in the absorption of infra-red radiations by rocksalt, we would not be justified in expecting the absorption data to show up the discrete character of the vibration spectrum very obviously. Even if theoretical considerations had permitted any such result, the low resolving powers used and the difficulties of observation in the remote infra-red would prevent its realisation. Some indications of the discrete structure of the spectra are however forthcoming from the work of Czerny (1930) and Barnes and Czerny (1931). These authors have studied the variation with wavelength in the reflecting power of a rocksalt plate at nearly normal incidence, and also the variations of the transmission coefficient with

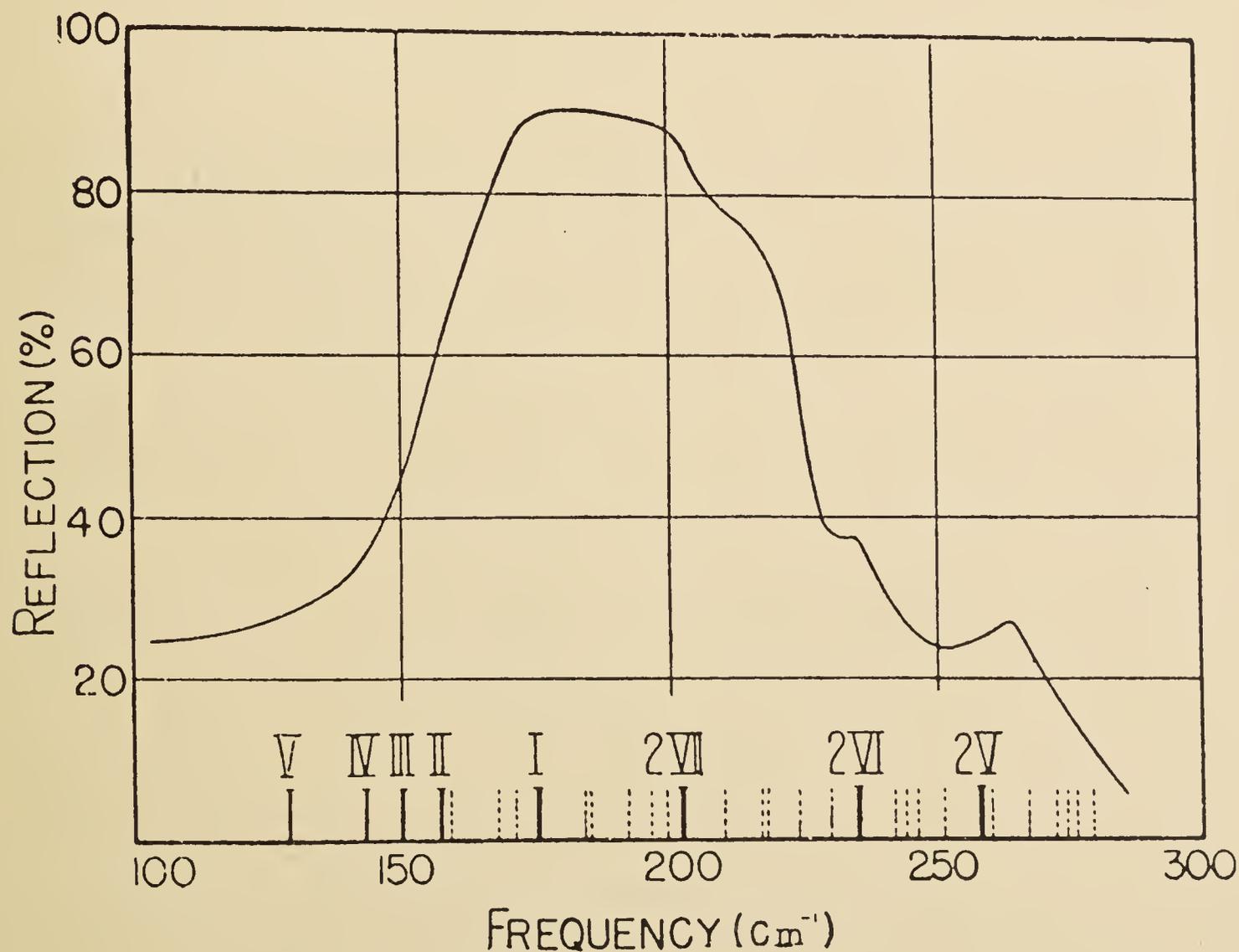


Figure 2. Reflecting power of a rocksalt plate.

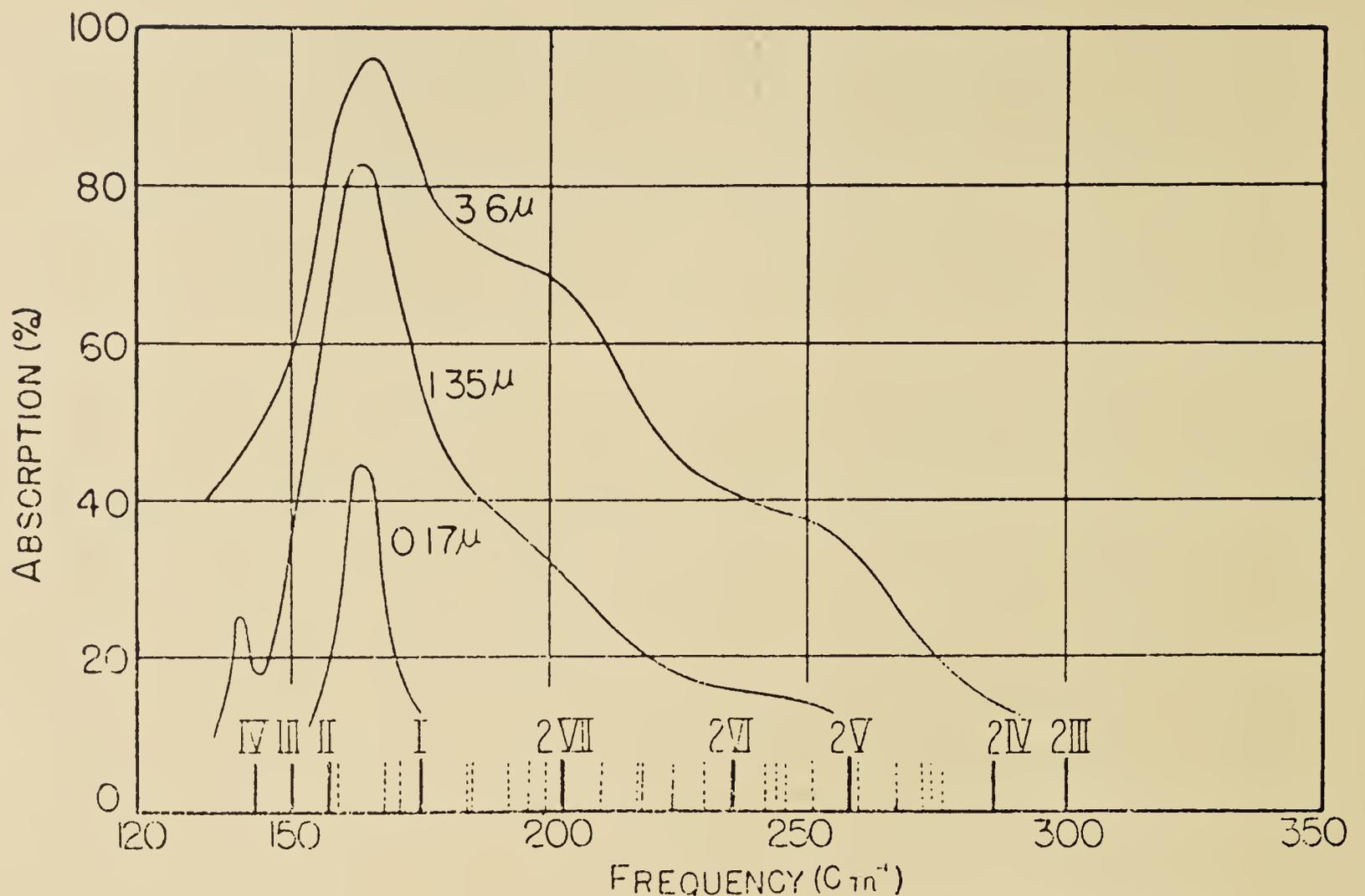


Figure 3. Absorption spectra of rocksalt films.

wavelength for plates of different thicknesses. Their results are shown in figures 2 and 3, carefully redrawn with wave-numbers instead of wavelengths as abscissae; for purposes of comparison, the fundamental vibration frequencies and their overtones have been indicated on the abscissae by heavy lines and the various possible combinations by dotted lines. It will be seen from figure 2 that the reflecting power rises steeply and reaches its maximum value at the point where the first-order vibration spectrum ends. The fall of the reflecting power in the region of the second-order spectrum is less abrupt and shows undulations, the positions of which roughly agree with the overtone frequencies of our modes VII, VI and V.

It is a noteworthy feature in figure 3 that the "peak" of absorption even with the thinnest films does not coincide with the frequency of the oscillation of the Na^+ and Cl^- lattices with respect to each other which is our mode III, but is shifted definitely to a higher frequency. The explanation of this effect is evidently that besides mode III, there are other modes, viz., I and II, and also various combinations in the vicinity which are active, and the course of the absorption curve is determined by the superposition of all their activities. The subsidiary maximum at 143 cm^{-1} noticed in the absorption curve for the second thinnest film may be identified with the fundamental frequency of mode IV. With the thickest of the three films, undulations are noticed in the absorption curve at

approximately the same frequencies as the octaves of modes VII and V. Mentzel (1934) has recorded an inflexion in the absorption curve of rocksalt at about 290 cm^{-1} which may be interpreted as due to the activity of the overtones of modes III and IV.

8. Summary

It is pointed out that the vibration frequencies of the rocksalt structure are determined entirely by short-range atomic interactions, since the effects of the Coulomb forces cancel out. The numerical evaluation of the nine eigenfrequencies on this basis leads to results in excellent accord with the observational data. Their activities in light-scattering and infra-red absorption are also discussed. The vibration most strongly active in light-scattering is that of the Cl^- ions normal to the octahedral planes, the Na^+ ions remaining at rest. It is also pointed out that the peak of the infra-red absorption at $61\ \mu$ for thin films observed by Barnes and Czerny does *not* represent the frequency of oscillation of the Na and Cl lattices with respect to each other, but is shifted with respect to it owing to the activity of other modes in the vicinity.

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The vibration spectra of crystals—Part IV. Magnesium oxide

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2. Evaluation of the nine fundamental frequencies
3. Their infra-red activities
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1. Introduction

Magnesium oxide crystallises in the cubic system and X-ray diffraction studies show that its structure is similar to that of rocksalt. The high values of its density and elastic constants indicate, however, that the atomic interactions are far stronger in magnesium oxide than in rocksalt. This circumstance taken in conjunction with the low atomic weights of magnesium and oxygen has a notable influence on the vibration frequencies of the structure. Instead of being crowded together in the remote infra-red as in the case of rocksalt, the spectral frequencies are high and widely separated from each other and by the same token are very little influenced by thermal agitation. Magnesium oxide is accordingly a perfect choice for a material that would demonstrate by its spectral behaviour the monochromatic character of the atomic vibration frequencies in crystals. This indication of theory is strikingly borne out by the observations of Barnes and Brattain (1935) on its infra-red absorption spectrum. Employing plates of five widely different thicknesses obtained by cleavage from a large synthetically prepared single crystal, they recorded their absorption curves with a rocksalt spectrometer, using an amplifying arrangement which gave a 150-fold magnification of the galvanometer deflections. The results showed the presence of some 40 well-defined absorption lines between 6μ and 15.5μ , those of shorter wavelengths being most clearly exhibited by the thicker plates and those of longer wavelengths by the thinnest of the five plates.

In view of the similarity of structure, the nine fundamental frequencies of MgO may be evaluated with the aid of the same formulae as in the case of rocksalt considered in the preceding paper. The three fundamentals with the highest frequencies are found to fall within the region investigated by Barnes and Brattain, and their positions can be checked from the absorption curves published by these authors. The positions of the other six fundamentals as evaluated from the formulae find experimental support in the observations made by Strong (1931*a, b*) and by Fock (1934) in the region of wavelengths beyond the reach of a rocksalt spectrometer. The numerous other absorption lines noticed by Barnes and Brattain are evidently the overtones and summations of the nine fundamental frequencies.

2. Evaluation of the nine fundamental frequencies

Some idea of the magnitude of the forces which hold the magnesium and oxygen atoms together in the crystal may be obtained from the results of the analysis of the band spectra of MgO in the state of vapour (P C Mahanti 1932). The vibration frequencies as deduced from the "red" and "green" systems of bands are respectively 822 cm^{-1} and 812 cm^{-1} in the lower state and 668 cm^{-1} and 771 cm^{-1} in the upper state. We may reasonably expect to find frequencies of this order of magnitude also in the vibration spectrum of the crystal. Actually, all the investigators [Tolksdorf (1928), Fock (*loc. cit.*), Barnes and Brattain (*loc. cit.*)] have found a strong absorption at about $14.2\ \mu$ (704 cm^{-1}). Taking this to represent the fundamental of highest frequency, we may at once evaluate P, the larger of the two constants which we need to know. The second constant T may, as in the case of rocksalt, be expected to be quite small in comparison with P. The frequencies of the two lowest fundamentals are determined exclusively by the value of T, but as they are not directly accessible to observation, we have to choose T so as to fit the facts best over the whole range of the spectrum. Table 1 above shows the nine eigenfrequencies of MgO as calculated from the simplified formulae of the preceding paper, with the atomic weights of oxygen and magnesium substituted for those of sodium and chlorine. The values of P and T adopted are shown at the head of the table.

3. Their infra-red activities

If all the eigenvibrations are completely independent normal modes, only ν_3 which is the oscillating of the Mg and O lattices of atoms against each other would be active in infra-red absorption, and the rest would be inactive. As remarked already in the cases of diamond and rock-salt, such independence of the normal modes does not, as a matter of fact, subsist. On the other hand, there is clear evidence of the existence of a strong coupling between them due to

Table 1. Calculated eigenfrequencies of magnesium oxide
($P = 2.82 \times 10^5$ dynes per cm, $T = -0.05 \times 10^5$ dynes per cm, $m_H =$ mass of hydrogen atom.)

Designation	Description of mode	Degeneracy	$4\pi^2\nu^2c^2m_H$	Calculated frequency cm^{-1}	Calculated wavelength μ
ν_1	Normal oscillation of cubic planes, Mg and O atoms in same phase.	3	$0.1037P - 0.036T$	704	14.2
ν_2	Tangential oscillation of cubic planes, Mg and O atoms in opposite phases.	6	$0.1037P + 0.397T$	680	14.7
ν_3	Oscillation of Mg and O lattices in opposite phases.	3	$0.1037P + 0.830T$	652	15.35
ν_4	Normal oscillation of octahedral layers of O atoms, Mg being at rest.	4	$0.0625P - 0.5T$	584	17.1
ν_5	Tangential oscillation of octahedral layers of O atoms, Mg being at rest.	8	$0.0625P + 0.25T$	527	19.0
ν_6	Normal oscillation of octahedral layers of Mg atoms, O being at rest.	4	$0.0412P - 0.33T$	474	21.1
ν_7	Tangential oscillation of octahedral layers of Mg atoms, O being at rest.	8	$0.412P + 0.165T$	428	23.4
ν_8	Normal oscillation of cubic planes, Mg and O atoms in opposite phases.	3	$-0.794T$	258	38.8
ν_9	Tangential oscillation of cubic planes, Mg and O atoms in same phase.	6	$-0.397T$	184	54.4

anharmonicity and the finite amplitudes of vibration. As a consequence of this coupling, the activity of any mode results in an induced activity of the modes having frequencies not too greatly differing from it. On this basis, we should expect not merely ν_3 , but also the higher and lower frequencies to be active in infra-red absorption. ν_8 and ν_9 in the table may however be expected to be more or less completely inactive by reason of their very low frequencies in comparison with ν_3 .

Barnes and Brattain studied the reflecting power of an MgO crystal and found that it rises steeply from about $13\ \mu$ and shows a double maximum at $14.8\ \mu$ and $15.3\ \mu$ of about 65% in each case and then drops down again sharply. That the peak at $14.8\ \mu$ is itself the joint effect of more than one active frequency between $14\ \mu$ and $15\ \mu$ is clearly shown by their absorption curve for this region recorded with the thinnest of their five plates, as well as by that obtained with a layer of MgO fumed on to a plate of NaCl. As we shall see later, three summational frequencies ($\nu_5 + \nu_9$), ($\nu_7 + \nu_8$) and ($\nu_6 + \nu_9$) also fall in the vicinity, and it is therefore not surprising that a good deal of detail is observed in this region. There is however no difficulty in recognising the presence in the absorption curves of two closely adjacent fundamental frequencies at about $14.15\ \mu$ and $14.55\ \mu$ respectively besides a third at $15.35\ \mu$, in agreement with the indications of theory shown in table 1.

Strong (1931*a*) studied the transmission through a film of MgO of infra-red radiations of selected wavelengths obtained by means of crystal reflections. Table 2 exhibits his results.

In the same paper, Strong recorded the percentage of reflection by an MgO crystal at $22.9\ \mu$ and $32.8\ \mu$ as 80% and 33% respectively. In a later paper (1931*b*) he gives fresh determinations over these and many more wavelengths, and these are listed in table 3. The results obtained by Strong, viz., practically complete absorption for 20.75 and $22.9\ \mu$, and nearly total reflections at the same wavelengths are what should be expected if there are fundamental frequencies at $21.1\ \mu$ and $23.4\ \mu$ as shown in table 1. The practically complete transparency for longer wavelengths and the near identity of the reflecting power for such wavelengths with the theoretical value of 27% given by the dielectric constant 9.8

Table 2. Percentage transmission by MgO film

Wavelength in μ	6.7	8.7	20.75	22.9	27.3	29.4	32.8
Percentage transmission	88	36	04	02	90	93	87

Table 3. Percentage reflection from MgO crystal

Wavelength in μ	20.7	23	27.3	29.4	32.8	41	52	63
Percentage reflection	80	72	44	42	35	33	32	31

are also significant. They are fully consistent with the *absence* of any fundamental frequency between 24μ and 38μ and the *inactivity* of the two lowest frequencies at 38.8μ and 54.4μ respectively.

Since Strong's observations indicate that the fundamental frequencies at 21.1μ and 23.4μ are strongly active, and since this activity is an induced effect, we should expect the fundamentals at 17.1μ and 19.0μ appearing in table 1 to be still more strongly active, especially the one at 17.1μ in view of its being adjacent in frequency to the "active" third fundamental. This indication is strikingly supported by the observations of Fock (1934). This author, working with a film of MgO found that by far the strongest absorption in the whole wavelength region between 2μ and 40μ is at the wavelength 17.3μ , and that the absorption falls off rapidly both towards longer and shorter wavelengths. This observation shows clearly enough that 17.3μ is very close to an active fundamental. But it seems at first sight rather surprising that the activity of ν_4 should exceed that of ν_3 so notably. It may be recalled, however, that in the case of rocksalt, a similar situation but in the opposite direction arises, viz., the peak of infra-red absorption by thin films is situated at ν_1 instead of at ν_3 . One may therefore hazard the suggestion that the explanation is the same in both cases, the reversal as between NaCl and MgO being due to the fact that the metallic atom is the lighter in one case and the heavier in the other.

It may be remarked that no direct observation of the two lowest fundamentals ν_8 and ν_9 is possible since they are inactive. The fifth fundamental ν_5 falls on the steeply rising part of the transmission curve of Fock but is not indicated by any distinct peak of absorption. It is to be presumed therefore that its activity is rather low, possibly for the same reason that the activity of ν_4 is very high.

4. Analysis of the absorption curves

The range of wavelengths covered by the observations of Barnes and Brattain includes besides 3 out of the 9 fundamentals, also 7 out of the 9 octaves, 34 out of the 36 possible summations of the frequencies taken two at a time, and nearly all of the 93 frequencies appearing in the third-order spectrum. It might seem at first sight scarcely possible to analyse an absorption spectrum including such a crowd of distinct frequencies. Various factors however simplify the task considerably, especially since the nine fundamental frequencies are known in advance with some precision. Firstly, the fundamental of highest frequency and its overtones fix the upper limits of frequency for the successive orders of spectra. Expressed in infra-red wavelengths, these limits are 14.2μ , 7.1μ and 4.7μ respectively. We do not therefore have to look for any fundamentals between 14.2 and 7.1μ or for second-order lines between 7.1μ and 4.7μ . Intensity considerations are also very helpful. In a particular region of the spectrum, a fundamental may be expected to appear more strongly than an octave, an octave more strongly than a summation

of two frequencies, a second-order frequency more strongly than one of the third-order, and so forth. Considerations of this kind are strongly supported by the observations recorded with the five plates of widely different thicknesses which enable us to assess the activity in absorption of the various frequencies. Comparison of the different absorption curves shows, for instance, that with the thinnest plate of all (0.075 mm), the first-order spectrum is strongly developed, the second-order spectrum appears rather weakly and the third-order spectrum still more weakly. With the next thicker plate (0.12 mm), the first-order is completely blocked out, the second-order is very strongly developed, and the third-order is quite definitely present. With the plate of thickness 0.47 mm, the second-order spectrum is blocked out for wavelengths greater than 10μ , but for the

Table 4. Calculated and observed absorption frequencies

Sl. no.	Plate thickness	Wavelength observed	Frequency observed	Assignment	Calculated frequency
	mm	μ	cm^{-1}		cm^{-1}
1	0.075	15.4	651	ν_3	652
2	0.075	15.2	658	$\nu_6 + \nu_9$	658
3	0.075	14.7	680	ν_2	680
4	0.075	14.4	694	$\nu_7 + \nu_8$	686
5	0.075	14.2	704	ν_1	704
6	0.075	14.0	714	$\nu_5 + \nu_9$	711
7	0.075	13.8	725	$\nu_6 + \nu_8$	732
8	0.075	13.1	763	$\nu_4 + \nu_9$	768
9	0.075	12.8	781	$\nu_5 + \nu_8$	785
10	0.075	12.1	826	$\nu_3 + \nu_9$	836
11	0.12	11.7	855	$2\nu_7$	856
12	0.075	11.6	862	$\nu_2 + \nu_9$	864
13	0.12	11.15	897	$\nu_1 + \nu_9$	888
14	0.12	10.9	917	$\nu_6 + \nu_7$	902
15	0.075	10.7	935	$\nu_2 + \nu_8$	938
16	0.12	10.5	952	$2\nu_6$	948
17	0.075	10.2	980	$\nu_1 + \nu_8$	962
18	0.12	10.0	1000	$\nu_5 + \nu_6$	1001
19	0.12	9.5	1053	$2\nu_5$	1054
20	0.12	9.3	1075	$\nu_3 + \nu_7$	1080
21	0.12	9.0	1111	$\nu_4 + \nu_5$	1111
22	0.075	8.8	1136	$\nu_1 + \nu_7$	1132
23	1.75	8.7	1149	$\nu_2 + \nu_6$	1154
24	0.12	8.5	1177	$2\nu_4$	1168
25	0.12	8.3	1205	$\nu_2 + \nu_5$	1207
26	1.75	8.15	1227	$\nu_1 + \nu_5$	1231
27	0.12	7.9	1266	$\nu_2 + \nu_4$	1264
28	0.47	7.6	1316	$2\nu_3$	1304
29	1.75	7.3	1370	$2\nu_2$	1360
30	3.05	7.1	1408	$2\nu_1$	1408

wavelengths between $7\ \mu$ and $9\ \mu$ where all the absorptions are necessarily weak, the observations with this plate as well as with the still thicker plate ($1.75\ \text{mm}$) are distinctly helpful.

The octaves of the fundamental frequencies are those most easily recognised in the absorption curves, and their observed positions furnish welcome confirmation of the correctness of the theoretically determined fundamental frequencies. $2\nu_7$, $2\nu_6$, $2\nu_5$ and $2\nu_4$ are seen very clearly in the absorption curve of the plate $0.12\ \text{mm}$ thick. $2\nu_7$ is indicated by a complete cut-off in a small region of wavelengths on either side of $11.7\ \mu$. $2\nu_6$ is indicated by a very prominent dip in the curve at $10.5\ \mu$. $2\nu_5$ is marked by a sharp and fairly prominent absorption line at $9.5\ \mu$. $2\nu_4$ may also be made out at $8.5\ \mu$, but appears much better developed as a deep trough at that position with the next thicker plate ($0.47\ \text{mm}$). A trough appears in the same curve at $7.6\ \mu$ which is the position of $2\nu_3$. A dip at $7.3\ \mu$ in the absorption curve for the plate of $1.75\ \text{millimetre}$ thickness may be identified with $2\nu_2$, and the dip at $7.1\ \mu$ in the absorption curve of the thickest plate with $2\nu_1$.

The second-order combinations are much more numerous than the octaves, and hence it is not quite so easy to identify their appearance in the absorption curves. Especially, however, in the case of the two thinnest plates where the confusion arising from the superposition of the still more numerous third order combinations is not so serious, assignments may be made of the features observed in the absorption curves with some measure of confidence. Table 4 is a collected list of 30 absorption lines in the first and second order spectra with their respective interpretations in terms of the nine fundamental frequencies.

5. Summary

The nine fundamental frequencies of the magnesium oxide structure are theoretically evaluated. Expressed as infra-red wavelengths, they are respectively 14.2 , 14.7 , 15.35 , 17.1 , 19.0 , 21.1 , 23.4 , 38.8 and $54.4\ \mu$. All except the last two are active in the infra-red and their positions check very closely with the absorptions observed by Barnes and Brattain, by Strong and by Fock. The octaves of the first seven fundamentals and numerous summational frequencies including also the two inactive fundamentals have been identified with the lines recorded by Barnes and Brattain in the absorption spectrum of cleavage plates of various thicknesses.

Note added, 26th November 1947—Deutschbein (*Annalen der Physik*, 1932, 14 712) found that a small percentage of chromic oxide can be successfully incorporated in MgO, thereby causing it to become luminescent when irradiated. The spectrum of this luminescence with the phosphor at room temperature, as also when it is cooled down to $-195^\circ\ \text{C}$ has been investigated by him. At room temperature, a strong emission appears at $\lambda\ 6991$ in the red, with subsidiary bands symmetrically disposed about it on either side. These bands are due to the combination of the

electronic transition at λ 6991 with vibrational transitions in the MgO structure, as is proved by the fact that at low temperatures the bands at shorter wavelengths vanish, while those at longer wavelengths persist. As the result of the cooling the principal emission shifts to λ 6981 and becomes sharper, while the bands appearing at longer wavelengths are resolved into a group of lines of varying intensities and widths in close juxtaposition. Other weaker electronic lines are also noticed in the vicinity of λ 6981. These are found to be stronger with some samples of the luminescent material than with others differently prepared. Deutschbein's data for the samples which do *not* show these weaker lines at room temperature indicate that *all the subsidiaries exhibited at liquid air temperature* (other than the weak electronic transitions) are due to combination of the principal emission at λ 6981 with vibrational transitions in the MgO structure. The eigenfrequencies of MgO thus deduced are found to agree closely with the frequencies theoretically derived in the present paper. The diffuseness of the vibrational lines is accounted for by the width of the electronic line and the loading of the MgO lattice by the heavy atoms of chromium.

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The vibration spectra of crystals—Part V. Lithium and sodium fluorides

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1. Introduction
2. Evaluation of eigenfrequencies.
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1. Introduction

Lithium and sodium fluorides are cubic crystals, their structure being of the NaCl type. The evaluation of their eigenfrequencies and the explanation of their spectroscopic behaviour are of particular interest for two reasons. Firstly, the low atomic weights of both the metal and the halogen and the strong interactions between the atoms in these fluorides result in their vibration spectra appearing at shorter wavelengths than with all the other alkali halides. Secondly, as the result of the disparity in atomic weights of metal and halogen in lithium fluoride, the modes in which the fluorine atoms alone oscillate have much lower frequencies than those in which the lithium atoms alone or both lithium and fluorine atoms together oscillate. The atomic weights of sodium and fluorine do not differ so widely, and hence there is a closer approximation to each other of the various eigenfrequencies in the case of sodium fluoride. The spectroscopic behaviour of the two fluorides differs notably as the result of these circumstances.

2. Evaluation of the eigenfrequencies

As in the cases of NaCl and MgO, the nine eigenfrequencies can be calculated from the simplified theoretical formula containing only two force-constants, one

Table 1. Eigenfrequencies of lithium fluoride
 ($P = 1.02 \times 10^5$ dynes/cm, $T = -0.015 \times 10^5$ dynes/cm, m_H is the mass of the hydrogen atom.)

Designation	Description of mode	Degeneracy	$4\pi^2 c^2 m_H \nu^2$	Infra-red wavelength
ν_1	Normal oscillation of the cubic planes with <i>Li</i> and <i>F</i> atoms in same phase	3	$0.197P - 0.34T$	16.9μ
ν_2	Tangential oscillation of the cubic planes with <i>Li</i> and <i>F</i> atoms in opposite phases	6	$0.197P + 0.62T$	17.5μ
ν_3	Oscillation of <i>Li</i> and <i>F</i> lattices in opposite phase	3	$0.197P \pm 1.58T$	18.2μ
ν_4	Normal oscillation of <i>Li</i> atoms in octahedral planes with <i>F</i> atoms at rest	4	$0.144P - 1.15T$	19.0μ
ν_5	Tangential oscillation of <i>Li</i> atoms in octahedral planes with <i>F</i> atoms at rest	8	$0.144P + 0.58T$	20.7μ
ν_6	Normal oscillation of <i>F</i> atoms in octahedral phase with <i>Li</i> atoms at rest	4	$0.0527P - 0.42T$	31.4μ
ν_7	Tangential oscillation of <i>F</i> atoms in octahedral planes with <i>Li</i> atoms at rest	8	$0.0527P + 0.21T$	34.2μ
ν_8	Normal oscillation of cubic planes with <i>Li</i> and <i>F</i> atoms in opposite phase	3	$-1.23T$	56μ
ν_9	Tangential oscillation of cubic planes with <i>Li</i> and <i>F</i> atoms in same phase	6	$-0.62T$	80μ

Table 2. Eigenfrequencies of sodium fluoride
 ($P = 6.82 \times 10^4$ dynes/cm, $T = -0.10 \times 10^4$ dynes/cm, m_H is the mass of the hydrogen atom.)

Designation	Description of mode	Degeneracy	$4\pi^2 c^2 m_H \nu^2$	Infra-red wavelength
ν_1	Normal oscillation of cubic planes with Na and F atoms in same phase	3	$0.0961P - 0.01T$	30.0μ
ν_2	Tangential oscillation of cubic planes with Na and F atoms in opposite phases	6	$0.0961P + 0.38T$	30.9μ
ν_3	Oscillation of Na and F lattices in opposite phase	3	$0.0961P + 0.77T$	31.9μ
ν_4	Normal oscillation of F atoms in octahedral planes with Na atoms at rest	4	$0.0526P - 0.42T$	38.3μ
ν_5	Tangential oscillation of F atoms in octahedral planes with Na atoms at rest	8	$0.0526P + 0.21T$	41.8μ
ν_6	Normal oscillation of Na atoms in octahedral planes with F atoms at rest	4	$0.0435P - 0.35T$	42.2μ
ν_7	Tangential oscillation of Na atoms in octahedral planes with F atoms at rest	8	$0.0435P + 0.17T$	45.9μ
ν_8	Normal oscillation of cubic planes with Na and F atoms in opposite phases	3	$-0.76T$	87μ
ν_9	Tangential oscillation of cubic planes with Na and F atoms in same phase	6	$-0.38T$	125μ

of which is much larger than the other. The large constant P is practically fixed by the highest of the nine eigenfrequencies, while the small constant T completely determines the two lower frequencies and notably influences also the intermediate ones. P can be found at once, while T is so chosen as to fit the spectroscopic facts best over the whole range of observation. Table 1 shows the evaluation for the case of lithium fluoride and table 2 for the case of sodium fluoride, the values of P and T being in each case shown at the head of the table.

3. Absorption and reflection by lithium fluoride

Reinkober (1926) made some observations on the reflection and absorption of radiations in the near infra-red by lithium fluoride in the form of plates obtained by compressing the powder under high pressure. Later, Barnes (1932) studied the absorption curves in the remote infra-red by very thin films of the substance. The absorption, reflection and dispersion by single crystals have been investigated over a wide range of wavelengths by Korth (1932) and by Hohls (1937). As the result of these various studies, we have a picture of the spectroscopic behaviour of lithium fluoride which can be interpreted in the light of the theoretical results.

Table 1 shows that 16.9μ is the shortest wavelength in the first-order spectrum. 8.5μ and 5.6μ would therefore be the shortest wavelengths respectively in the second-order and third-order spectra of overtones and summations of the fundamental frequencies. We should accordingly expect a large increase in the absorption coefficient in passing from 5.6μ to 8.5μ and a further very large increase in passing from 8.5μ to 16.9μ . The absorption measurements made by Hohls for various wavelengths and thicknesses fully support these indications of theory. Between 16μ and 35μ is a region of intense opacity as is to be expected. Hohls found a very weak but measurable transmission at 39μ and a notably larger transmission at 41μ . The measurements likewise show that a steep rise in the reflecting power starts at about 14μ and that a maximum of 78% is reached at 17μ . The reflection coefficient then diminishes a little and shows a minimum of 72% at 20μ . Beyond this wavelength it increases again and reaches a maximum value of 92% at 28μ . It then diminishes rapidly to 60% at 37μ and to 38% at 40μ , beyond which the fall is more gradual. The measurements of absorption in very thin films made by Barnes likewise show that the strongest absorption is in the region of wavelengths between 30μ and 35μ , the peak appearing at 32.6μ .

The facts recited above are readily understood on the basis that the first seven of the nine fundamentals listed in table 1 are rendered strongly active by reason of their coupling with the so-called "active" mode ν_3 , with the result that the whole range of wavelengths between 16.9μ and 34.2μ is one of intense opacity. The sixth and seventh fundamentals ν_6 and ν_7 represent the oscillations of the fluorine atoms against each other, the lithium atoms remaining at rest. Whereas the first reflection maximum between 15μ and 20μ is evidently due to the first five fundamentals which approximate to each other in frequency and form a group by

themselves, the second reflection maximum between 20μ and 40μ is evidently due to ν_6 and ν_7 , as also to various overtones and summations of the fundamental frequencies falling within this wavelength range. It is evident from the appearance of this second maximum of reflection, as well as from the fact that the strongest absorption by thin films is at 32.6μ approximately midway between ν_6 and ν_7 , that these two fundamentals are strongly active and indeed more so than any of the fundamentals of higher frequency. This is a remarkable but not altogether surprising result, since in the case of MgO we found that the oscillations of the oxygen atoms against each other give the maximum of infrared absorption. The explanation of the effect is presumably the same as in the case of MgO.

4. Absorption and reflection by sodium fluoride

The observations by Korth (*loc. cit.*) and by Hohls (*loc. cit.*) with crystal plates and of the absorption in thin films by Barnes (*loc. cit.*) give us the necessary data for the case of sodium fluoride. The clue to their understanding is likewise furnished by the activity of the eigenvibrations listed in table 2. In the present case, owing to the nearness of the atomic weights of sodium and fluorine, the four eigenfrequencies ν_4 , ν_5 , ν_6 and ν_7 form a group with their wavelengths 38.3μ , 41.8μ , 42.2μ and 45.9μ fairly close to each other. Their octaves likewise form a close group, the wavelengths being 19.2μ , 20.9μ , 21.1μ and 23μ . The absorption by thin films is a maximum at 40.6μ , approximately midway between ν_4 and ν_5 which represent the oscillations of the fluorine atoms with the sodium atoms at rest. In this respect, the behaviour of sodium fluoride is analogous to that of lithium fluoride. On the other hand, there is only one reflection maximum instead of two as in lithium fluoride within the range of wavelengths covered by the first-order spectrum. This maximum of 90% is located at 35μ and is evidently the resultant effect of all the seven active fundamentals. The increase in reflecting noticed for wavelengths greater than 20μ with a maximum of 48% at about 23μ in the second-order spectrum is evidently due to the group of octaves lying in the vicinity. The increase in the absorption coefficient between 19μ and 24μ observed by Hohls is likewise due to the same cause. No such effects are noticed with lithium fluoride, since in the latter case, $2\nu_7$ lies within the first-order spectrum, while $2\nu_6$, $2\nu_5$ and $2\nu_4$ are widely separated from each other in the second-order spectrum. Hohls has however observed a minor peak in absorption at about 12.9μ which may be ascribed to several summationals falling in that region.

5. Summary

The eigenfrequencies of lithium and sodium fluorides have been theoretically evaluated and their observed spectroscopic behaviour is found to be in accord

with the results. The greater disparity in the atomic weights of metal and halogen in the case of lithium fluoride than in sodium fluoride leads to some interesting differences in behaviour between the two substances. In both cases, however, the frequency of maximum absorption does *not* correspond with the oscillation of the metal and halogen atoms against each other, but agrees with that of the oscillations in which only the fluorine atoms move, the metal atoms remaining at rest.

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The vibration spectra of crystals—Part VI. Sylvine

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1. Introduction

The optical behaviour of sylvine shows clearly that the characteristic frequencies of atomic vibration lie more remotely in the infra-red than in the case of rock-salt. The question whether this is due solely to the atomic weight of potassium being greater than that of sodium or whether it is also partly due to a diminution in the strength of the interatomic forces is a point of considerable interest. The infra-red behaviour of sylvine has been studied by several investigators very thoroughly and their results furnish the data needed to decide this question. We shall accordingly proceed to evaluate the eigenfrequencies and to consider them in relation to the experimental facts. It may be remarked that some as yet unpublished work by Dr R S Krishnan on the second-order spectrum of light-scattering in sylvine has assisted in determining the appropriate values of the force-constants.

2. The nine eigenfrequencies of sylvine

As the atomic weight of chlorine is less than that of potassium, the two modes in which the chlorine atoms alone oscillate would have a higher frequency than the corresponding two modes in which the potassiums alone vibrate. The difference in atomic weights (35.5 and 39) is however not large, and it follows that the frequencies of these four modes would not differ very much from each other and that the sequence in which they appear would depend on the precise values of the force constants. Table 1 shows the calculation of the frequencies. The values of P and T are both a little smaller than for rock-salt. For convenience, the symbols ν_4 and ν_5 have been used to designate the oscillations of the chlorine atoms while ν_6 and ν_7 designate those of the potassium atoms. It will be noticed, however, that ν_6 is greater than ν_5 .

Table 1. Eigenfrequencies of KCl
 ($P = 2.30 \times 10^4$ dynes per cm; $T = -0.05 \times 10^4$ dynes per cm)

Designation	$4\pi^2 c^2 m_R^2 v^2$	Frequency cm^{-1}	Wavelength μ
v_1	$0.0538P + 0.00T$	145	69
v_2	$0.0538P + 0.214T$	138	72
v_3	$0.0538P + 0.430T$	132	76
v_4	$0.0282P - 0.226T$	114	89
v_5	$0.0282P + 0.113T$	100	100
v_6	$0.0256P - 0.205T$	108	93
v_7	$0.0256P + 0.102T$	95	105
v_8	$-0.429T$	60	167
v_9	$-0.214T$	43	233

3. The infra-red behaviour of sylvine

The so-called "fundamental" oscillation in which the potassium and chlorine atoms move in opposite phases is v_3 in our table, corresponding to an infra-red wavelength of 76μ . It is to be remarked that this does not coincide either with the "rest-strahlen" wavelength of 63.4μ with the wavelength of 70.7μ at which the maximum absorption is exhibited by the thinnest films (Barnes 1932). It will be noticed that the latter is nearer v_1 which has a wavelength of 69μ . These remarks reinforce the point that owing to the anharmonicity and the mutual coupling of the various eigenvibrations, all of them must be considered to be active in greater or less degree, and that we must take account also of the activity of the various overtones and summations of the nine fundamental frequencies. On this basis, it is possible to understand the facts established by experimental study regarding the infra-red behaviour of sylvine.

Czerny (1930) investigated the reflecting power over the entire range of infra-red wavelengths for which sylvine is opaque in moderate thicknesses. He found a small but quite definite swell in reflecting power in the wavelength range between 42μ and 48μ with a maximum of 20% at 46μ . Referring to table 1, we recognize that this is the region in which the octaves of the fourth, fifth and sixth eigenfrequencies are grouped together, and the increase of reflection is therefore to be ascribed to their presence and conjoint effect. At 48μ , the reflecting power reaches a minimum of 18% and then rises again steadily, reaching a maximum of about 90% in the range of wavelengths 60–65 μ . It then falls down to 78% at 70μ , 65% at 75μ , 45% at 80μ , 32% at 85μ and 26% at 90μ . The large increase in reflecting power in the range between 50μ and 70μ is a particularly noteworthy feature, and is readily understood when we recall that in this region lie numerous

frequencies in the second-order spectrum, viz., $2\nu_7$, $(\nu_6 + \nu_9)$, $(\nu_5 + \nu_9)$, $(\nu_4 + \nu_9)$, $(\nu_3 + \nu_9)$, $(\nu_2 + \nu_9)$, $(\nu_1 + \nu_9)$, $(\nu_7 + \nu_8)$, $(\nu_6 + \nu_8)$, $(\nu_5 + \nu_8)$, $(\nu_4 + \nu_8)$, $(\nu_3 + \nu_8)$ and $(\nu_2 + \nu_8)$. The fairly rapid drop of reflecting power at about $80\ \mu$ is an indication that the infra-red activity is considerable only for the three highest fundamentals ν_1 , ν_2 , ν_3 and is relatively small for the fundamentals of lower frequency. The behaviour of sylvine in this respect is closely parallel to that of rock-salt.

Mentzel (1934) has very elaborately investigated the absorption coefficient of sylvine plates of various thicknesses over a wide range of wavelengths. His work confirms the existence of the variations which we should expect in the range between $40\ \mu$ and $45\ \mu$ owing to the presence of the octaves of ν_3 , ν_4 and ν_6 in that vicinity. The large drop in the absorption coefficient which occurs between $34\ \mu$ and $23\ \mu$, and again between $23\ \mu$ and $17\ \mu$ is also readily understood, since $34\ \mu$, $23\ \mu$ and $17\ \mu$ are respectively the shortest wavelengths in the second-order, third-order and fourth-order spectra.

4. Summary

The nine eigenfrequencies of sylvine are evaluated, and it is shown that the wavelength at which the maximum absorption is exhibited by very thin films is much nearer the first than the third of them which is the so-called active oscillation of the potassium against the chlorine atoms. The absorption and reflection data over the whole range of wavelengths are in general accord with the indications of the theory. The force-constants for sylvine are a little smaller than for rock-salt.

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The infra-red spectrum*

1. Introduction

The radiations whose wavelengths are greater than those of visible light and less than those of the shortest radio-waves constitute the so-called “infra-red spectrum”. They are of great interest in relation to several subjects, as for instance, astrophysics, meteorology, thermodynamics and chemistry, to mention no others. The experimental study of the infra-red spectrum presents peculiar difficulties. For the most part, the aid of photography which makes exact studies possible with other parts of the electromagnetic spectrum is not available here. Less satisfactory devices have, therefore, to be employed, which mostly depend on the thermal or heating effect of the rays. As indicated by the Planck radiation formula, the energy of thermal radiation falls off rapidly with increasing wavelength. This makes it difficult to obtain sources of adequate strength for the larger wavelengths and renders observation and measurement with such wavelengths difficult and uncertain. A further problem is that of finding suitable materials for prisms which are transparent and have adequate dispersive power in the region under study. Absorption by water-vapour and by carbon dioxide in the atmosphere presents other complications. The necessity of exploring the spectrum step by step also makes the work laborious and time-consuming. It is not surprising that in these circumstances our knowledge of the infra-red spectrum has progressed much less quickly than that of the visible or ultraviolet. That such difficulties have been surmounted and useful results obtained by the pioneers in the field is a tribute alike to their experimental skill and to their perseverance.

A quickened interest in infra-red spectroscopy is evident at the present time. This is shown by the increased output of literature and also by the several excellent treatises which have appeared of recent years dealing with the field. These developments have doubtless been stimulated by the knowledge which has become available to us since 1928 by spectroscopic investigations on the scattering of light. When monochromatic radiations traverse a transparent medium, the spectrum of the diffused light exhibits new lines, the frequency shifts of which with respect to the incident light represent the characteristic infra-red

*Presidential Address delivered by Sir C V Raman, Kt., F.R.S., N.L., at the 13th Annual Session of the Indian Academy of Sciences, held at Cuttack, on the 26th December 1947.

frequencies of the substance. This way of finding the infra-red frequencies enables us to enlist the powerful aid of photography, since the shifted lines appear in the visible or ultra-violet region of the spectrum; whether the frequency shifts are large or small, they are recorded and rendered accessible to study with the same facility. The insight and knowledge thus derived have proved a powerful stimulus to further study of the infra-red absorption spectra and furnished aid in the interpretation of the results. The infra-red frequencies determined by either method being those of the molecular vibrations in the substance, the two methods are complementary to each other, and also mutually helpful. Quite appropriately, therefore, the results of both methods of study are discussed together in the most recent texts dealing with this field.

It is worthwhile emphasising that studies of the molecular vibration spectra by infra-red absorption or by the scattering of light are not merely of academic interest. Indeed, they have proved to be powerful aids to industry in the chemical and other allied fields. Especially in dealing with organic chemicals are such physical methods more convenient and – with appropriate techniques – also quicker than purely chemical methods of identification or analysis. The vibration spectrum of a molecule is determined by the geometric configuration of the atoms in it, as well as by the atomic masses and the binding forces holding them together. In consequence, the characteristic features of molecular structure reveal themselves by the vibration frequencies, as also by the intensities with which they appear in the infra-red spectra. Hence, the features of the observed vibration spectra are a powerful aid to the identification of the individual substances and to the quantitative analysis of mixtures.

2. Crystals and the infra-red spectrum

Crystals have played a notable part in the development of infra-red spectroscopy. We have only to recall the fact that the materials which are or could be utilized as dispersive prisms in infra-red work are crystals. The optical behaviour of such materials in relation to their chemical nature and physical structure offers much food for thought. Taking, for instance, the case of rock-salt, the measurements of its refractive index which have been made in the region of wavelengths between 1μ and 22μ indicate that the vibration frequencies which effectively determine its dispersion lie in the remote infra-red in the region of 60μ . We may well ask, why is it then that rock-salt begins to show an appreciable absorption at 12μ and exhibits a practically complete cut-off beyond 15.5μ making it useless as a material for prisms beyond that wavelength? Lithium fluoride again, which is another material which has lately come into use for infra-red work, has its effective “dispersion” frequency located at about 32μ . Nevertheless the material shows total opacity beyond 16μ . We are led to ask, what is the reason for such opacity?

Standing in close relation to the questions raised above, is the remarkable

discovery made by Rubens and Nichols that a beam of infra-red radiation is monochromatised more or less perfectly if it undergoes a series of reflections at the surface of a crystal. This method of obtaining "residual rays" by crystal reflections has been extremely useful in infra-red studies, as it enables a strong beam of specified wavelength to be readily obtained. Various questions arise with regard to the principle of the method. What relation does the residual-ray wavelength bear to the infra-red frequencies which are effective in dispersion? What thickness of the material is needed to give the desired strength of reflection? What is the relationship between the reflecting power and the absorption coefficient for wavelengths lying in the region of opacity?

It is evident that the answers to the questions raised above are closely related to the fundamental problem of the nature of the vibration spectrum of a crystal and its activity in infra-red absorption. This, in its turn connects up with the question of the relationship between the atomic architecture of the crystal and its infra-red activity. The intimate nature of this relationship will be evident when we consider for instance, the striking difference in behaviour between, say, diamond and rock-salt. The infra-red activity of diamond is extremely weak, while that of rock-salt is extremely strong. Is this difference in behaviour due merely to the difference in the details of crystal architecture, or is it due to the difference in the nature of the binding forces in the two cases?

The power of infra-red spectroscopy to throw light on the problems of crystal structure is strikingly exemplified in the case of diamond. As mentioned above, the infra-red activity of this crystal is weak, and a thickness of the order of one millimeter is needed to exhibit a readily measurable absorption. Remarkably enough, however, it has been found that the nature of the absorption curve is not the same in all diamonds. The majority of diamonds exhibit an absorption curve of the type shown in figure 1 in which there is a region of strong absorption between 700 cm^{-1} and 1500 cm^{-1} , while other diamonds (not so common) do *not* show the absorption in this region. All diamonds, however, show the absorption in the region of higher frequencies beyond 1500 cm^{-1} , and the features of such absorption do *not* show any noticeable differences as between different diamonds. The latter fact makes it clear that the strong absorption between 1500 cm^{-1} and 2900 cm^{-1} is a characteristic property of diamond. Why then is the absorption between 700 cm^{-1} and 1500 cm^{-1} present in some diamonds and absent in others? The answer to this question is furnished by the fact that the diamonds which show the absorption are those which exhibit the highest degree of homogeneity when examined by various optical and X-ray methods and which accordingly make the nearest approach to ideal perfection of crystal structure. *Per contra*, the diamonds which do not show the absorption show a visibly laminated structure when examined on the Federov stage under a polarizing microscope, and also various other properties indicating a notable heterogeneity of structure. It follows that the appearance of the infra-red absorption with the diamonds exhibiting it cannot be ascribed to the presence of crystal imperfec-

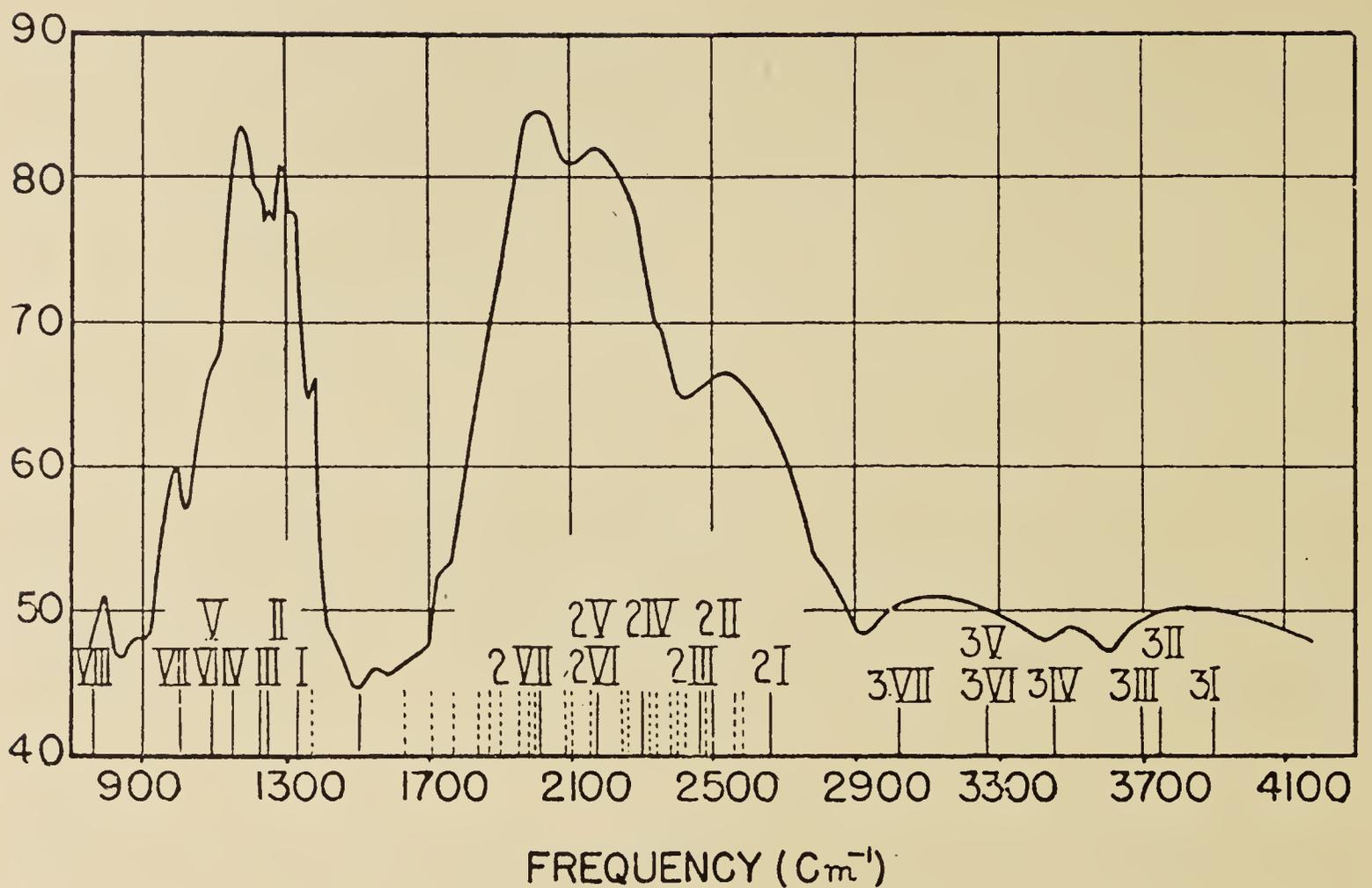


Figure 1. Infra-red absorption spectrum of diamond (after K G Ramanathan)

tions, but must be referred to a fundamental difference in crystal symmetry between the two classes of diamonds, which results in an observable infra-red activity of the vibrations of the structure in one case and its inactivity in the other.

3. The case of magnesium oxide

We shall now proceed briefly to recount the facts which have come to light as the result of experimental studies on the infra-red behaviour of magnesium oxide. Thin films of this substance are readily obtained by deposition of the fumes from burning magnesium, or alternatively by evaporation in a vacuum. Large single crystals of magnesium oxide have also been successfully prepared by solidification from the substance melted at over 2500°C in an electric furnace. The crystals belong to the cubic class, and can be readily cleaved into flat plates in the same manner as rock-salt. Using the material in various forms, several investigators (Tolksdorf 1928; Strong 1931; Fock 1934; as also Barnes and Brattain 1935) have investigated the behaviour of the substance in respect of infra-red absorption and reflection. The results reported by these authors are exceedingly remarkable, namely, that in spite of the simplicity of its structure which is similar to that of rock-salt the crystal has a whole series of characteristic infra-red frequencies in the vicinity of which intense absorption and reflection are observed. Tolksdorf observed a strong absorption at 14.2μ . Strong found

practically complete absorption at 20.8μ and at 22.9μ . He also found that at these wavelengths, the reflection coefficient was 80% and 72% respectively and fell off rapidly with larger wavelengths. Fock found the most intense absorption at 17.3μ which he regarded as characteristic of MgO, though his observations also gave indications of other absorption maxima both at longer and at shorter wavelengths. The most remarkable results of all were those of Barnes and Brattain. These authors studied the reflection coefficient of MgO over the whole range of wavelengths covered by a rock-salt spectrometer, and found a strong reflection between 13μ and 16μ with a double peak located at 14.8μ and 15.3μ respectively. Even more striking were the infra-red absorption curves in the wavelength range between 6μ and 15.5μ recorded by them with five plates of various thicknesses, ranging from the thinnest obtainable to very thick ones. The curves exhibit no fewer than 40 well-defined absorption *lines* in this range.

The facts recited above are irreconcilable with the idea regarding the spectroscopic behaviour of crystals derived from the lattice dynamics of Max Born as applied to various actual cases by Blackman, Kellermann and others. Since the structure of magnesium oxide is similar to that of rock-salt, the only mode of vibration of the structure which according to the theory of Born would be infra-red active is the so-called "fundamental vibration" of the lattices of magnesium and oxygen atoms against each other. There would, in addition, be an immense number of other modes of vibration which taken together would constitute a continuous spectrum of frequencies. Actually, the observations indicate that the vibration spectrum of magnesium oxide in the region of infra-red frequencies is not continuous but discrete, consisting of a set of sharply defined monochromatic frequencies, all of which are infra-red active in greater or less degree.

4. The eigenvibrations of crystal structures

To find an explanation of the remarkable facts detailed above, we have to consider the fundamental problem of the nature of the vibration spectrum of a crystal. The older theories of the subject (Debye, Max Born) approach this from the standpoint of the classical theory of elasticity. They identify the vibrations in the solid with waves traversing its interior in all directions. Such an approach is legitimate in considering the vibrations of low frequency in respect of which the discrete atomic structure of the medium may be ignored and the medium treated as continuous. But in considering the behaviour of a crystal in the infra-red range of frequency, we have necessarily to take into account its discrete structure, and the experimental facts show that the identification of the atomic vibrations with waves of all possible lengths and directions filling the volume of the crystal is not a valid procedure, and that a different approach to the problem is necessary. The fact that the crystal consists of a great many units of very small size which are

exactly similar and similarly situated is the very natural starting point for such an approach. Since further, the atomic forces which determine the modes and frequencies of vibration of these units of structure are of limited range, the problem of determining these modes and frequencies is closely analogous to the theory of the vibrations of polyatomic molecules, except that the units of structure are not isolated from each other and hence it is necessary to consider also their interactions. The problem has been handled by the present writer from this point of view (1943, 1947) and the result is reached that the structure of a crystal containing p atoms per unit cell has $(24p - 3)$ characteristic eigenvibrations. In $(3p - 3)$ of these eigenvibrations, equivalent atoms in adjacent cells of the structure oscillate with the same amplitude and the same phase, while in the remaining $21p$ eigenvibrations they oscillate with the same amplitude but with a phase which alternates in successive cells along one, two or all axes of the crystal lattice. The maximum number of distinct eigenfrequencies is $(24p - 3)$, but this number may be considerably reduced by reason of the crystal symmetry in various actual cases. For crystals of the rock-salt type $p = 2$, and there are 45 eigenvibrations, but owing to the high crystal symmetry, many of these are similar and the number of distinct eigenfrequencies is only 9. Considered in relation to the entire crystal, these modes and frequencies are of course to be regarded as being very highly degenerate.

5. Evaluation of the eigenfrequencies

Exact expressions for the 9 eigenfrequencies of crystals of the rock-salt type have been obtained by Mr K G Ramanathan (1947). These expressions have been simplified and used by the present writer (1947) for theoretical evaluation of the frequencies for a number of crystals having this structure, including especially magnesium oxide. The eigenfrequencies of the four alkali halides with the lowest atomic weights as theoretically evaluated are shown on the wave-number scale in figure 3. The formulae as simplified contain four constants, P , P' , T and T' . But P and P' are nearly equal to each other and are large compared with T and T' . Hence, a further simplification may be effected by replacing P and P' by a single constant P and similarly also T and T' by a single constant T , being in each case their arithmetical mean. Even as thus highly simplified, the formulae are sufficiently accurate to represent the facts correctly. For instance, in the case of magnesium oxide, the 9 eigenfrequencies expressed in wave-numbers come out as 704, 680, 652, 584, 527, 474, 428, 258 and 184 cm^{-1} respectively. Expressed in infra-red wavelengths, they are 14.2μ , 14.7μ , 15.35μ , 17.1μ , 19.0μ , 21.1μ , 23.4μ , 38.8μ and 54.4μ . The first three of the calculated eigenfrequencies (ν_1, ν_2, ν_3) are recorded in the observations of Barnes and Brattain made with their thinnest plate as strong and well-defined absorption maxima. ν_4 coincides with Fock's absorption maximum, while ν_6 and ν_7 are those noted by Strong. The octaves of

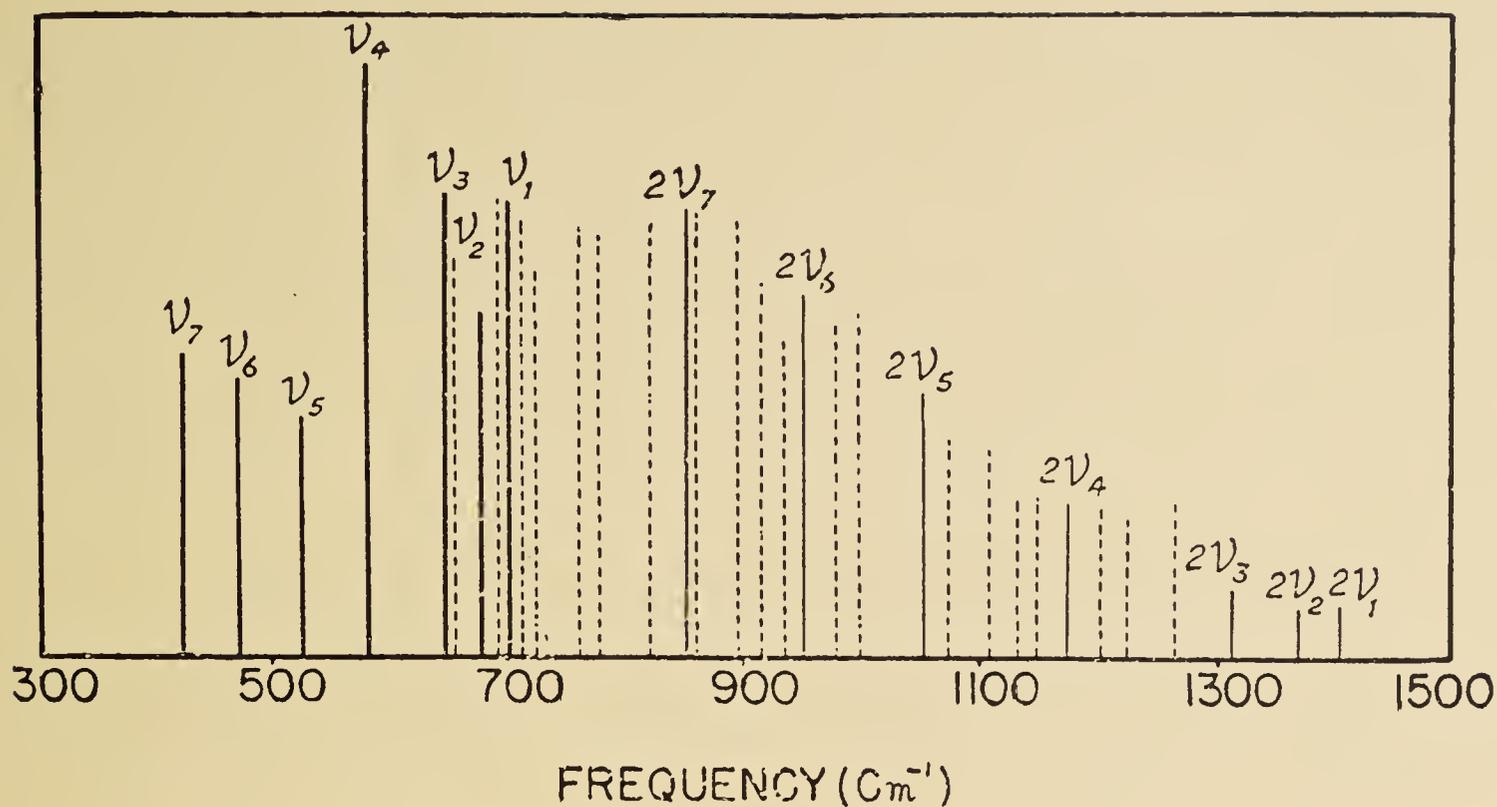


Figure 2. Infra-red absorption frequencies of magnesium oxide.

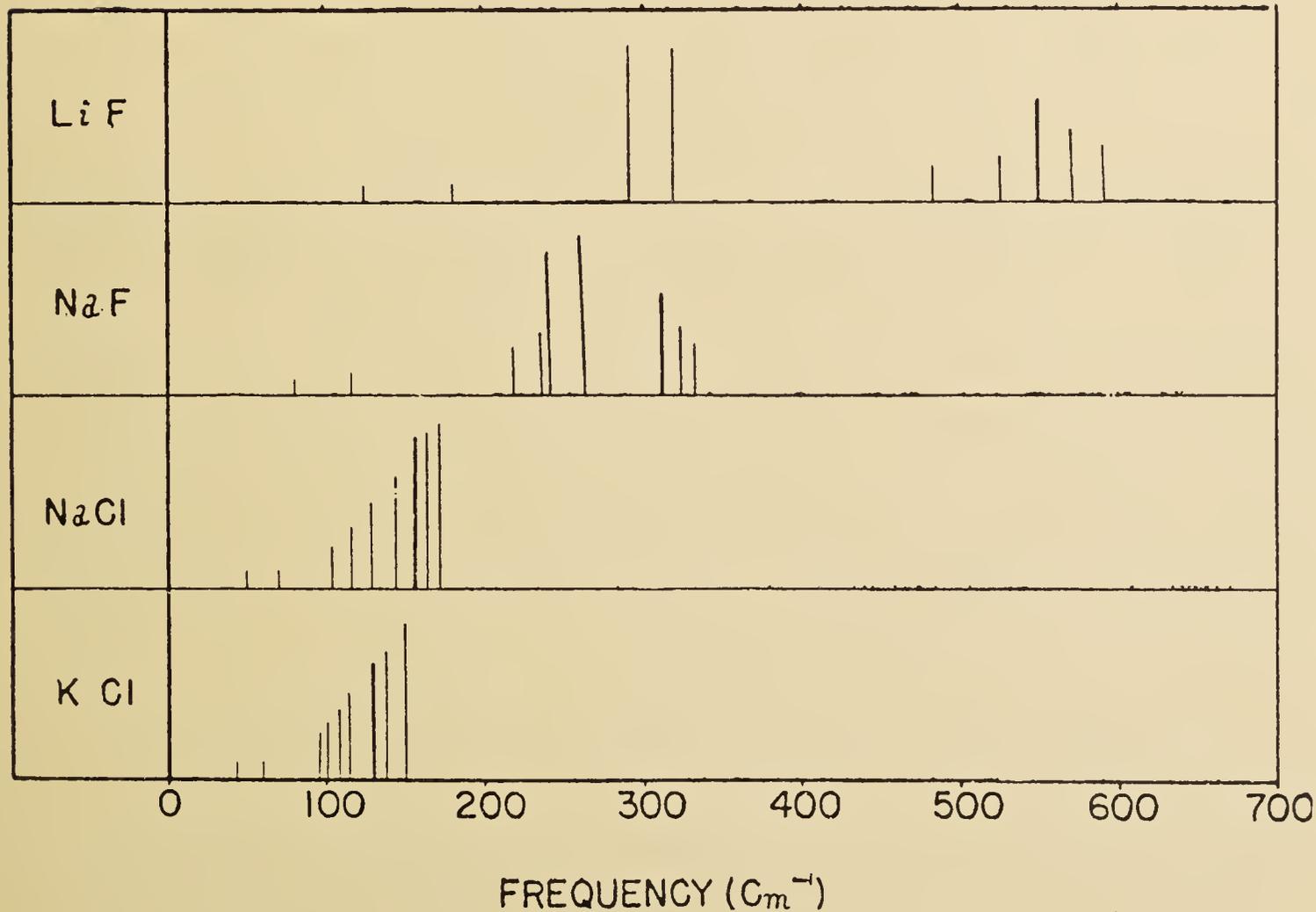


Figure 3. Eigenfrequencies of four alkali halides.

the first seven eigenfrequencies are also represented in the data of Barnes and Brattain as prominent absorption maxima. Some twenty other absorption lines recorded by them are also satisfactorily accounted for as summations of the eigenfrequencies taken two at a time. In figure 2 above, the fundamental eigenfrequencies are shown by heavy lines, their octaves by thin lines, and the summational frequencies by dotted lines. ν_8 and ν_9 are less than 300 cm^{-1} and do not therefore appear in the diagram.

It may be explained here that the constants P and P' represent the forces arising from unit displacements respectively of the two types of atoms in the structure from their positions of equilibrium, while T and T' represent the forces on a given atom due to a unit displacement of a neighbouring atom of the same kind. The magnitude of the constants is accordingly a measure of the strength of the interatomic forces which hold the crystal together. The following figures indicate how they differ in the five cases for which the frequency spectrum has been theoretically evaluated.

Table 1

Substance	P	T	Units
MgO	2.82×10^5	-0.05×10^5	dynes per cm
LiF	1.02×10^5	-0.015×10^5	„
NaF	6.82×10^4	-0.10×10^4	„
NaCl	2.422×10^4	-0.053×10^4	„
KCl	2.30×10^4	-0.05×10^4	„

The value of P in the case of magnesium oxide is of the same order of magnitude as the force-constants for covalent bindings known in various cases, and hence in spite of its structure being of the rock-salt type, magnesium oxide is very far indeed from being an "ionic" crystal. It may be mentioned for the sake of comparison that the force-constant P in the case of diamond is 7.54×10^5 dynes per centimeter. The force-constants in the two fluorides are distinctly smaller than in magnesium oxide, those for sodium fluoride being much less than for lithium fluoride. There is a further large fall in the magnitude of the force-constants in passing from the fluoride to the chloride of sodium, but only a trifling diminution as we pass from NaCl to KCl.

6. The eigenvibrations and their infra-red activity

The *third* highest eigenfrequency (ν_3) shown by a thick line in each case for the four alkali halides is that of the mode in which the metal and the halogen atoms move together as groups in opposite phases. (In the Born theory, this is the infra-red active frequency.) The eigenfrequencies ν_4 and ν_5 are those of vibrations in

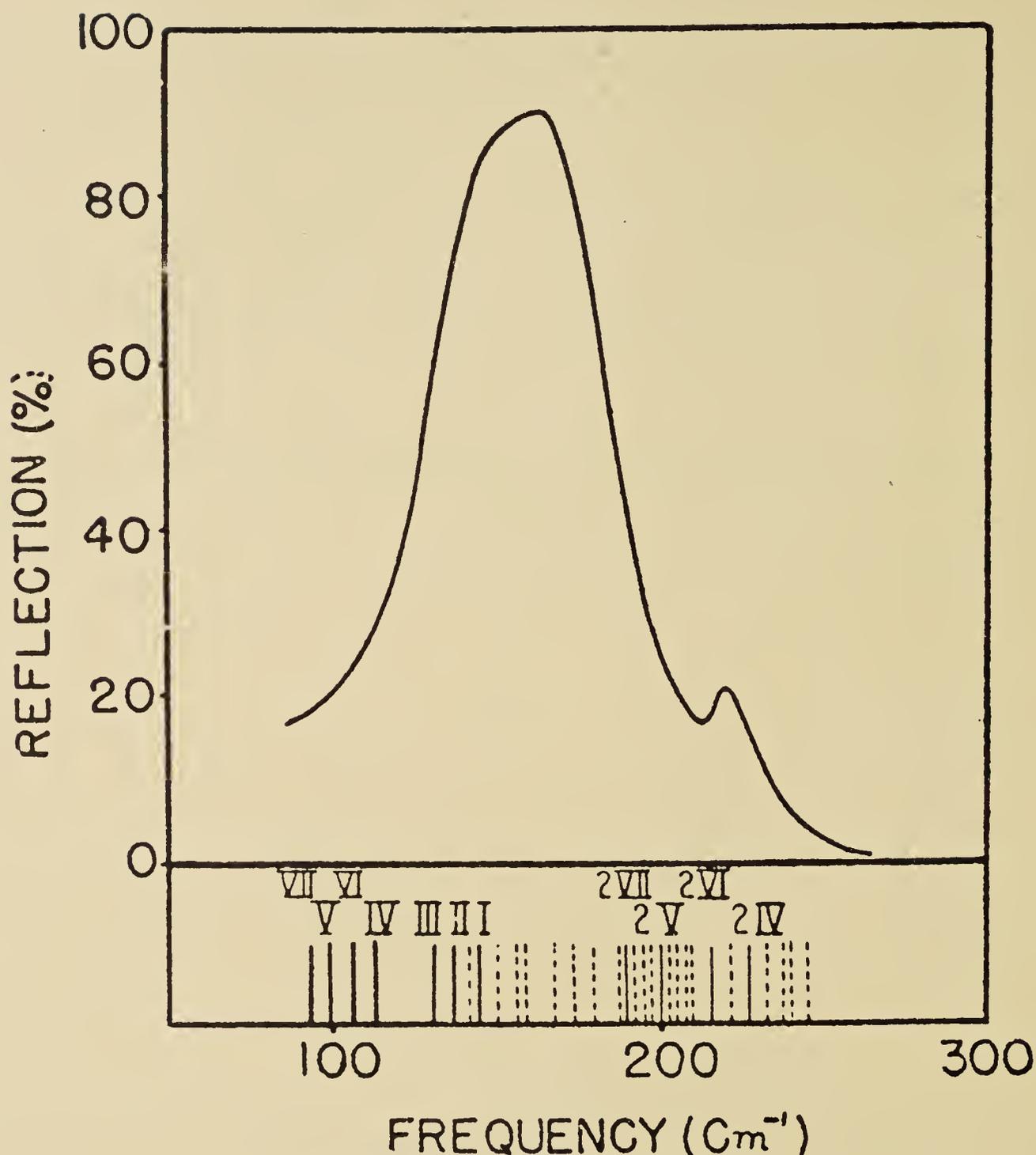


Figure 5. Reflection coefficients of potassium chloride.

distinct minimum. The reason for this behaviour, as will be seen from the figure, is that the fundamental eigenfrequencies fall into two widely separated groups. It is particularly remarkable that the group of lower frequency which does not include the so-called "active" fundamental ν_3 gives a stronger reflection than the group of higher frequency which includes ν_3 . A similar feature also appears in absorption. According to Barnes (1932), the strongest absorption by thin films of lithium fluoride is at 32.6μ which is midway between ν_6 and ν_7 whose infra-red wavelengths are respectively 31.4μ and 34.2μ . In other words, the strongest infra-red activity is *not* that of the mode in which the lithium atoms and the fluoride atom move as groups in opposite phases, but of the modes in which the fluorine atoms alone oscillate, the lithium atoms remaining at rest.

Surprising as the foregoing results may seem, they are supported by the fact that analogous results are also exhibited by the other crystals, though in a less

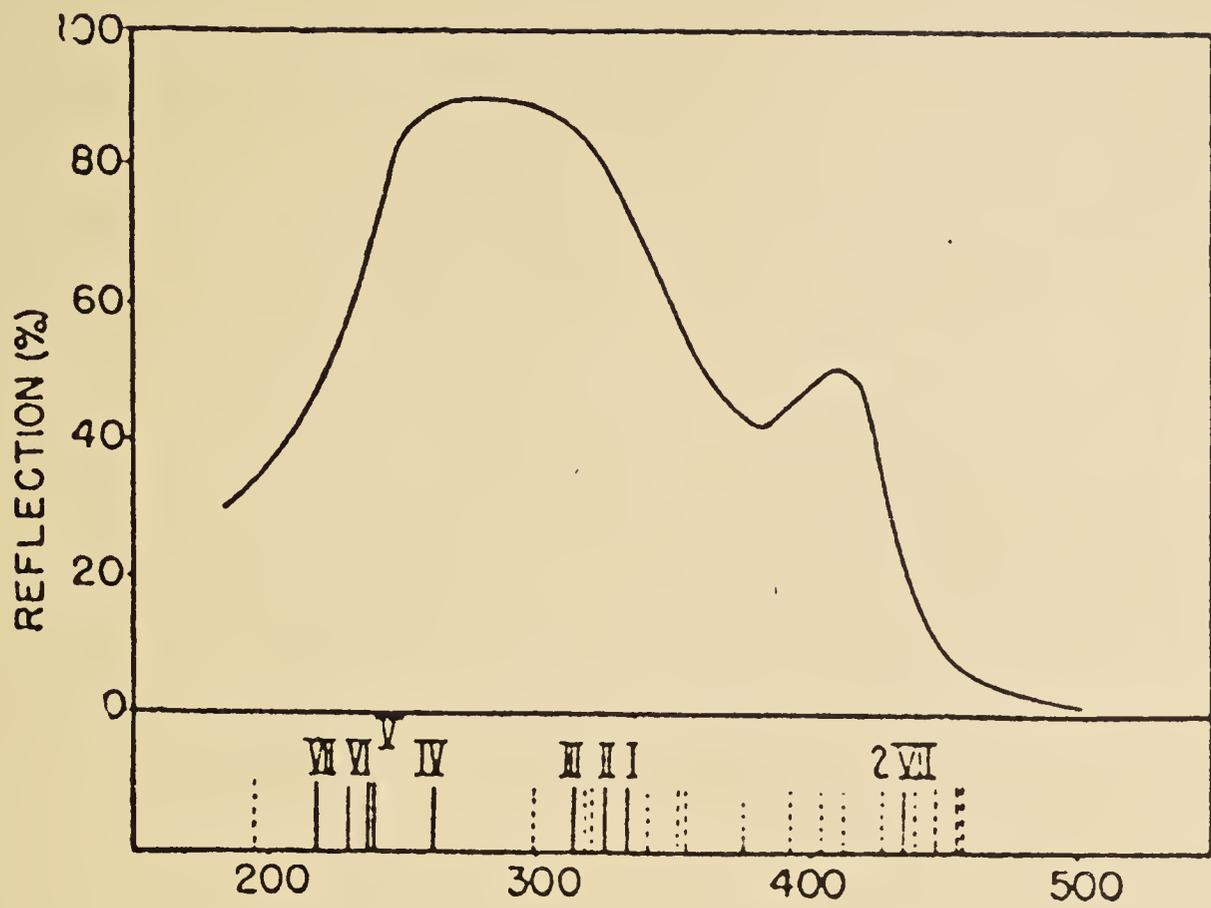


Figure 6. Reflection coefficients of sodium fluoride.

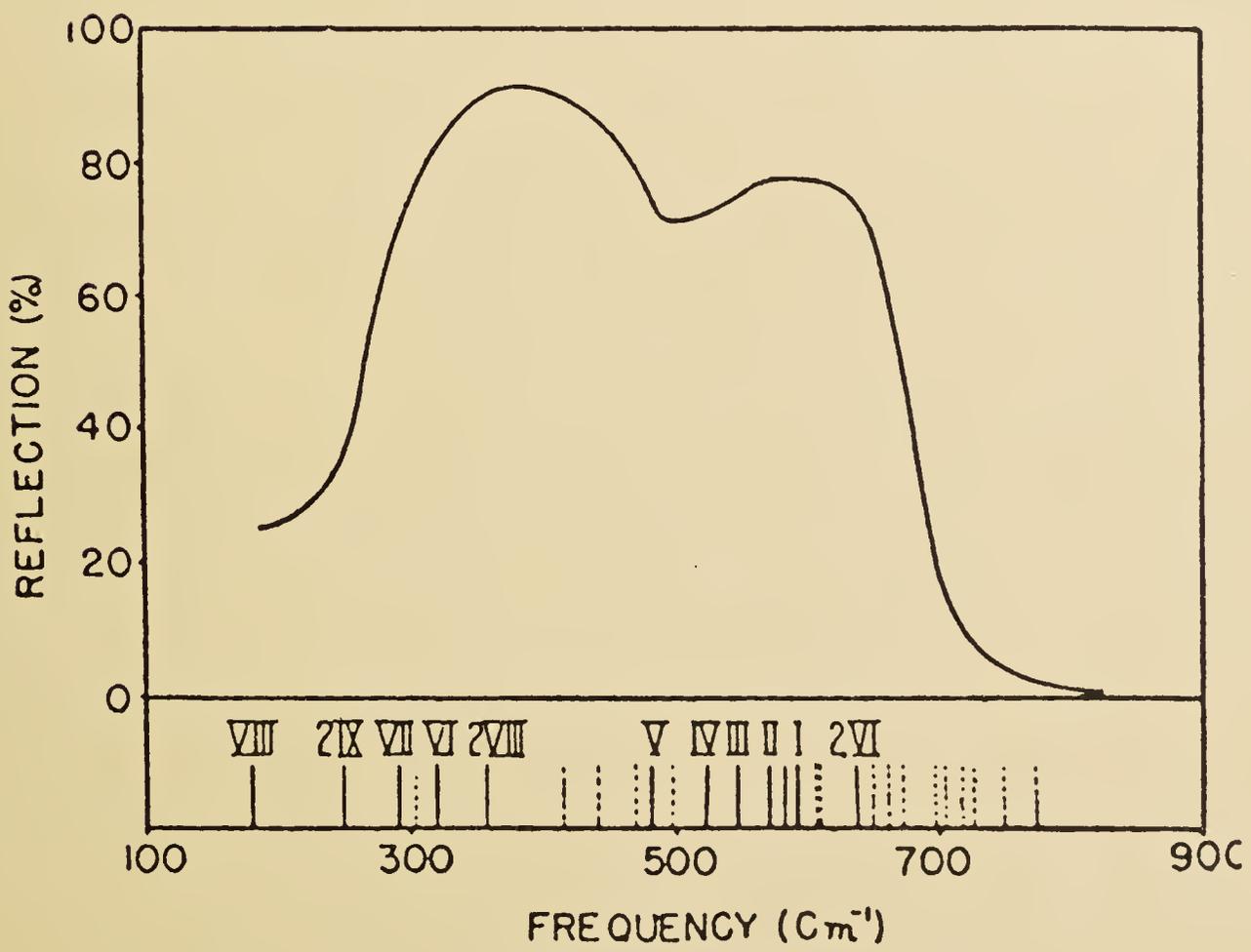


Figure 7. Reflection coefficients of lithium fluoride.

striking fashion. In the case of sodium fluoride, Barnes (1932) found the maximum absorption by thin films to be at 40.6μ , which is midway between 38.3μ and 41.8μ , the wavelengths of ν_4 and ν_5 which are oscillations of the fluorine atoms with the sodium atoms remaining at rest. With magnesium oxide, the strongest absorption by thin films as found by Fock is at 17.3μ , nearly coinciding with ν_4 which is an oscillation of the oxygen atoms against each other, the magnesium atoms remaining at rest. In the cases of NaCl and KCl, the maximum absorption by thin films does not coincide with ν_3 , but move nearly with ν_1 which is the highest of the nine eigenfrequencies, being an oscillation of the atomic layers parallel to the cubic planes, normally to themselves, with the metal and the halogen atoms which they contain moving in the same phase.

The fact which emerges clearly from the case of magnesium oxide is that all the eigenvibrations, as also their octaves and their summations, are infra-red active in greater or less measure. The measure of this activity is given by the absorption coefficient at the particular frequency. This has been evaluated by Mr K G Ramanathan from the published data of Barnes and Brattain (1935) and represented on a logarithmic scale of ordinates in figure 2. It will be seen that the absorption coefficient falls off rapidly as we move towards higher frequencies. This suggests that the infra-red activity of the various modes in MgO and in the alkali halides is essentially an induced effect, arising from mechanical anharmonicity and consequent coupling with each other of the various eigenvibrations, as a consequence of which all of them become active in greater or less measure, depending principally on their approximation in frequency to the "active" mode ν_3 . The activity of the various possible overtones and summations necessarily falls off as we pass successively from the first-order to the second-order spectrum and from the second-order spectrum to the third-order spectrum and so on, the successive limits of frequency of these spectra being set by the highest fundamental and its overtones. The large diminution in the absorption coefficient and consequent improvement in transparency as we move towards shorter wavelengths is readily understood on this basis.

Fuller details regarding the various topics referred to above, as well as references to the cited literature will be found in papers by the writer appearing in the *Proceedings of the Indian Academy of Sciences* for December 1947.

C V RAMAN

The eigenvibrations of crystal structures*

1. Introduction

As is well known, the atomic architecture of a crystal may be described as a three-dimensionally periodic distribution of matter in space on a very fine scale. The regularity of such arrangement is, however, liable to be disturbed in various ways and especially by the thermal agitation in the crystal or by the incidence of radiations on it, and the atoms then vibrate about their respective positions of equilibrium. A knowledge of the modes and frequencies of the vibrations thus arising is of the greatest possible importance for the theory of the solid state. For, it enables us to evaluate the strength of the interatomic forces and thus to obtain a quantitative physical picture of the structure of the crystal, supplementing the geometric description furnished by X-ray analysis. Further, such knowledge is the basis for a development of the theory of the physical properties of crystals, including especially all those which depend on or are influenced by the temperature of observation.

The volume of papers under review is intended to furnish a definitive answer to the problem of ascertaining the modes and frequencies of vibration of the atoms in a crystal in relation to their geometric distribution in space and the forces holding them together as a rigid structure. Of the 19 papers forming the symposium, 9 describe new experimental results obtained from investigations specially designed to throw light on this fundamental problem. These experimental papers are richly illustrated, no fewer than 65 separate spectrograms and 35 microphotometer records besides numerous diagrams being reproduced to aid the reader's understanding and appreciation of the results of the researches. The introductory paper of the symposium furnishes the necessary theoretical background, while the remaining nine papers are devoted to the consideration of the consequences of the theory in particular cases and their comparison with the facts of experiment. Before entering into a discussion of the theoretical aspects of the subject, it appears desirable to present the reader with a review of the experimental situation as it emerges from the symposium.

**Symposium of papers on the vibration spectra of crystals*, December 1947, 190 pp with 18 plates. Published by the Indian Academy of Sciences, Bangalore.

2. The scattering of light in crystals

Many investigations on the vibration spectra of crystals have been made during the past twenty years by the method first employed in 1928 by the present writer, viz., illuminating the crystal by monochromatic light and recording the spectrum of the scattered radiations emerging from it. While much empirical knowledge of value has accumulated as the result of such studies, they left untouched the fundamental problem of ascertaining what the *complete* vibration spectrum of any crystal is and of how it is related to the structure of the crystal. Investigations designed to resolve this problem were undertaken at Bangalore a few years ago by Dr R S Krishnan. Numerous crystals have been studied with the utmost possible thoroughness and a rich harvest of results obtained in every one of the cases investigated, viz., calcite, quartz, barytes, gypsum, fluorspar, corundum, topaz, diamond, rock-salt, sylvine, ammonium chloride, ammonium bromide. We shall presently proceed to take note of such of these studies as are now reported on. As an example of the results which previously found publication, we may mention the case of calcite, with which no fewer than 16 frequency shifts were recorded by R S Krishnan as against a maximum of 7 by earlier workers. The following facts observed with this crystal may be regarded as typical of those noticed with inorganic crystals generally. (a) The frequency shifts recorded with small or moderate exposures represent the *first-order* spectrum, namely, the fundamental eigenfrequencies of atomic vibration in the crystal which are active in light scattering. (b) In strongly exposed spectrograms, frequency shifts are recorded with appreciable intensity which represent the vibration-spectra of higher orders, viz., the overtones and summationals of the eigenfrequencies, including those not recorded as fundamentals. (c) The frequency shifts of all orders are recorded as

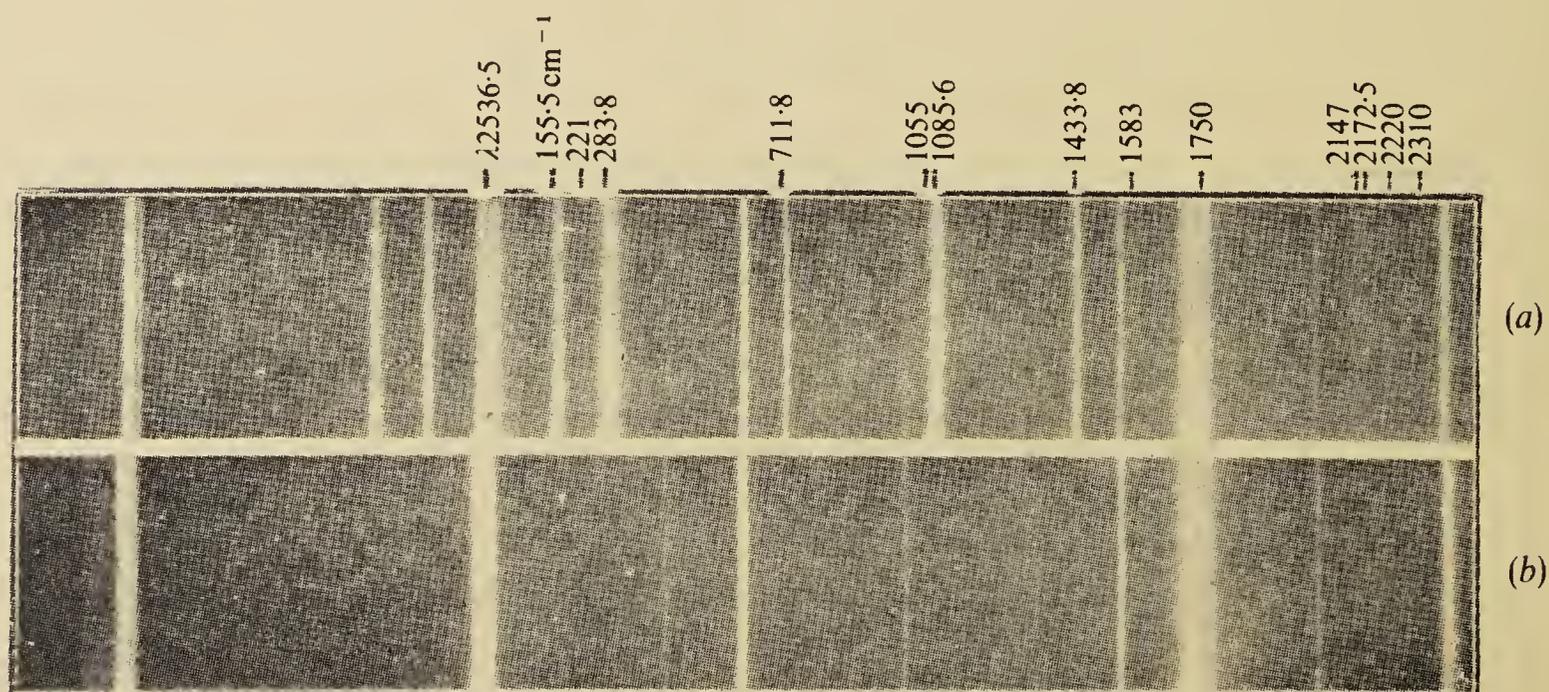


Figure 1. (a) Raman spectrum of calcite. (b) Mercury spectrum (after Dr R S Krishnan).

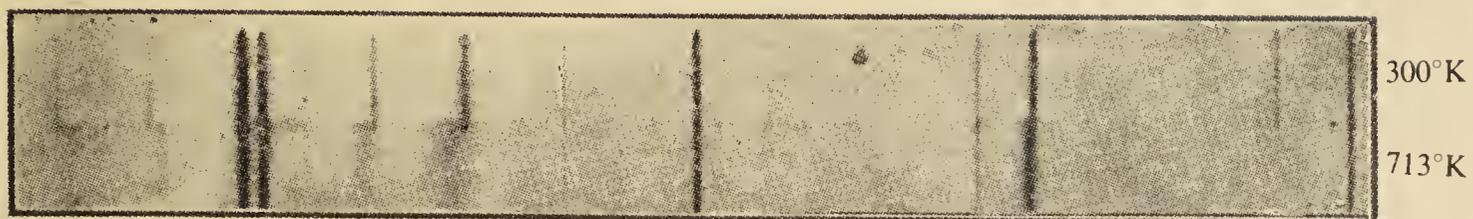


Figure 2. Variation with temperature of the Raman spectrum of calcite (after P K Narayanaswamy).

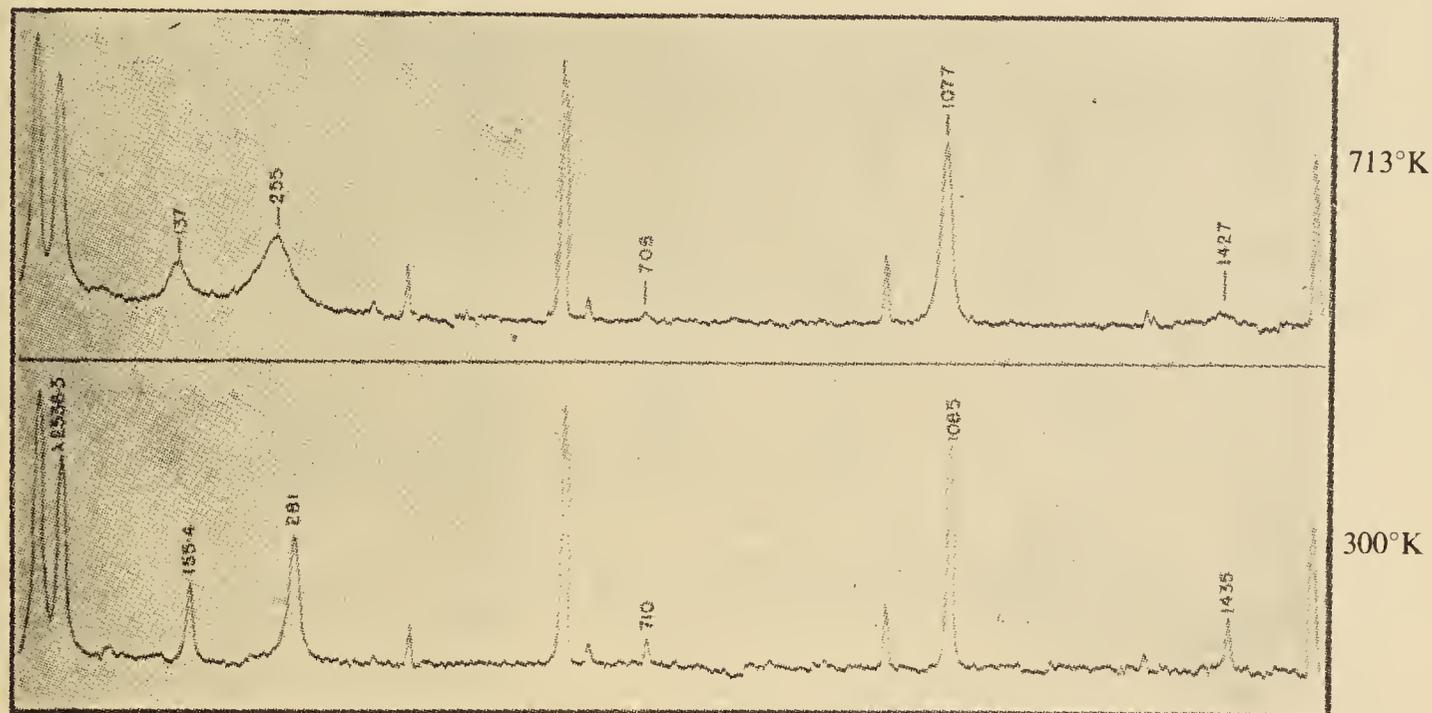


Figure 3. Microphotometer records of the Raman spectrum of calcite at two different temperatures (after P K Narayanaswamy).

sharply defined lines on a clear field, the apparent spectral width of such lines in many cases being no greater than that of the mercury arc lines registered on the plates with comparable intensities. (d) When the crystal is heated, the spectral lines broaden and shift towards the position of the exciting radiation and their peak intensities diminish notably. (e) Vice-versa, if the crystal is cooled to liquid-air temperature, the spectral lines sharpen and shift away from the exciting radiations while their peak intensities increase. But these effects are by no means so conspicuous as those of the opposite kind noticed on heating (see figures 1, 2 and 3).

3. The cases of corundum and topaz

These are two well known crystals found in nature, while the former can also be prepared synthetically. Corundum is of much simpler composition and structure than topaz, and is a crystal of the trigonal class, while topaz is orthorhombic. These differences are reflected in the degree of complexity of their vibration spectra, 7 frequency shifts being recorded by Dr R S Krishnan with corundum

and 32 with topaz, as compared with a maximum of 2 and 11 frequency shifts respectively reported by earlier authors. The lower crystal symmetry of topaz evidently results in a much larger proportion of the possible modes of vibration being active in light-scattering than in the case of corundum. Figure 4 reproduces, in part, the spectrogram of pure topaz obtained in light-scattering, while figure 5 is the *luminescence* spectrum of topaz containing a trace of chromic oxide

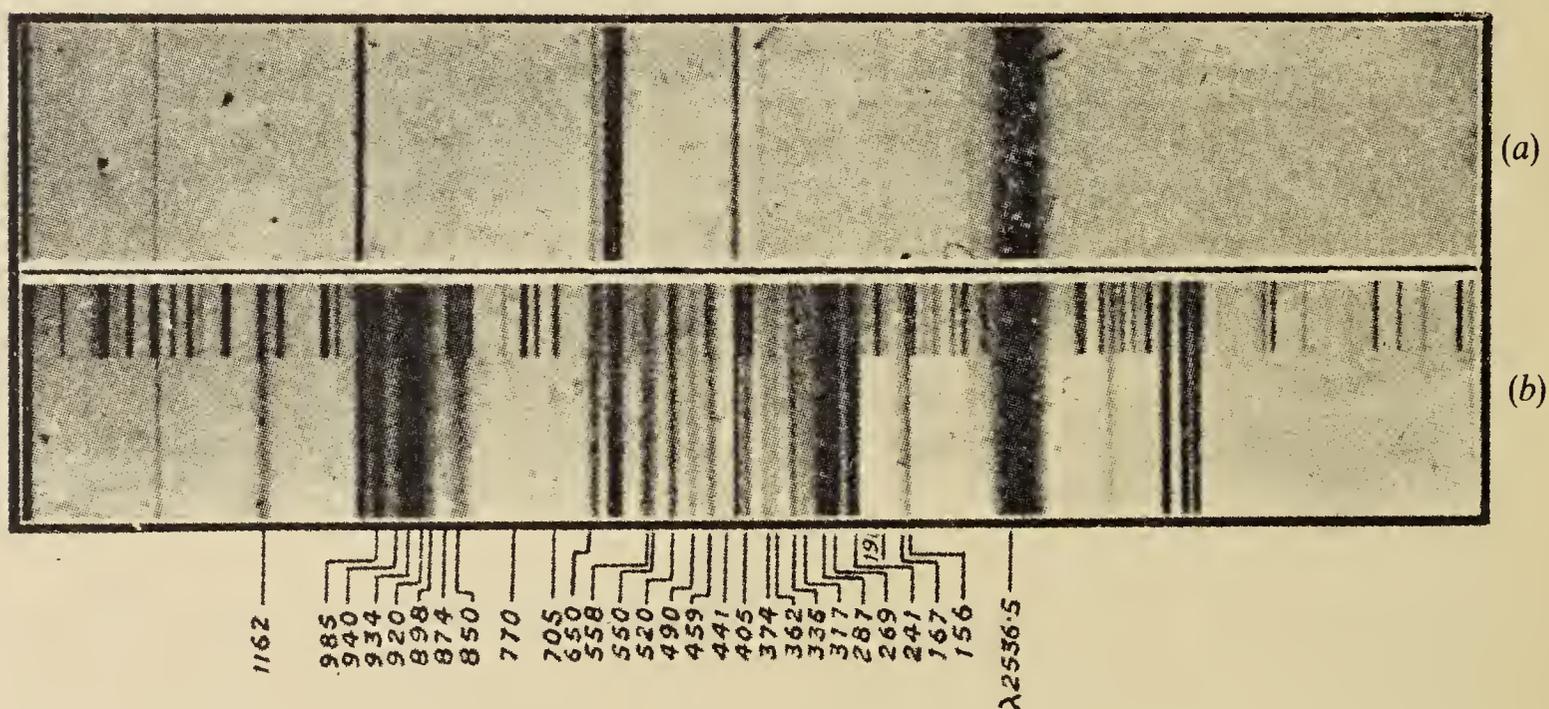


Figure 4. (a) Mercury spectrum. (b) Raman spectrum of topaz (in part) (after Dr R S Krishnan).

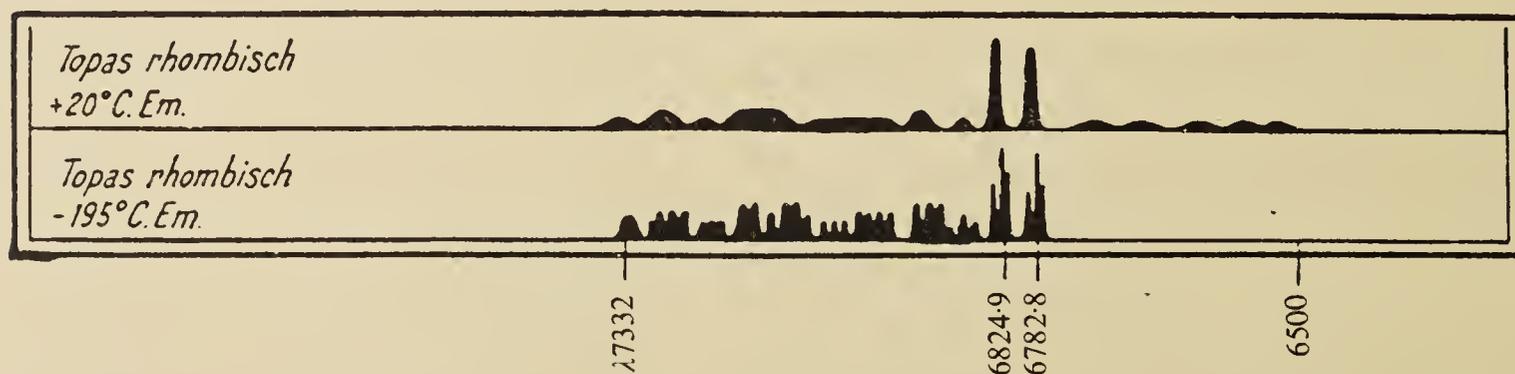


Figure 5. Luminescence spectrum of topaz (after Deutschbein).

as impurity recorded with the crystal held at liquid-air temperature. A comparison of the frequency shifts $\lambda 2536.5$ as observed in light-scattering and from $\lambda 6824.9$ (the principal chromium line) as observed in luminescence shows a most remarkable concordance. The bands observed in the luminescence spectrum of ruby and also those observed in its absorption spectrum are successfully explained on similar lines in terms of the vibration frequencies of the corundum crystal observed in light-scattering and in infra-red absorption.

It is obvious that the mechanism of the diffusion of light by a crystal and the mechanism of its impurity-activated luminescence are very far from being identical. That nevertheless there is a concordance between the vibration-spectra as observed by the two methods is theoretically significant. It indicates that the vibration spectrum of a crystal as observed in light-scattering is not fundamentally different in its general character from the *complete* vibration-spectrum. In other words, the latter is essentially a *line-spectrum* exhibiting a discrete set of frequencies. This conclusion is reinforced by a vast array of other evidence furnished by critical studies of the spectroscopic behaviour of numerous crystals by diverse methods reported in the literature during the last twenty years. It will not, however, be necessary for us to enter into a description or discussion of such evidence, since the facts regarding magnesium oxide discussed in *Current Science* for December 1947, and those regarding diamond and the alkali halides which we shall presently consider completely clinch the issue.

4. The case of diamond

Five of the papers in the symposium deal exclusively with the spectroscopic behaviour of diamond, and we may here briefly summarise their contents. Dr R S Krishnan reports, in continuation of his earlier studies, a thorough investigation on the scattering of light in diamond, examined spectroscopically. The frequency shifts observed are of three kinds as indicated against them in figure 6; the

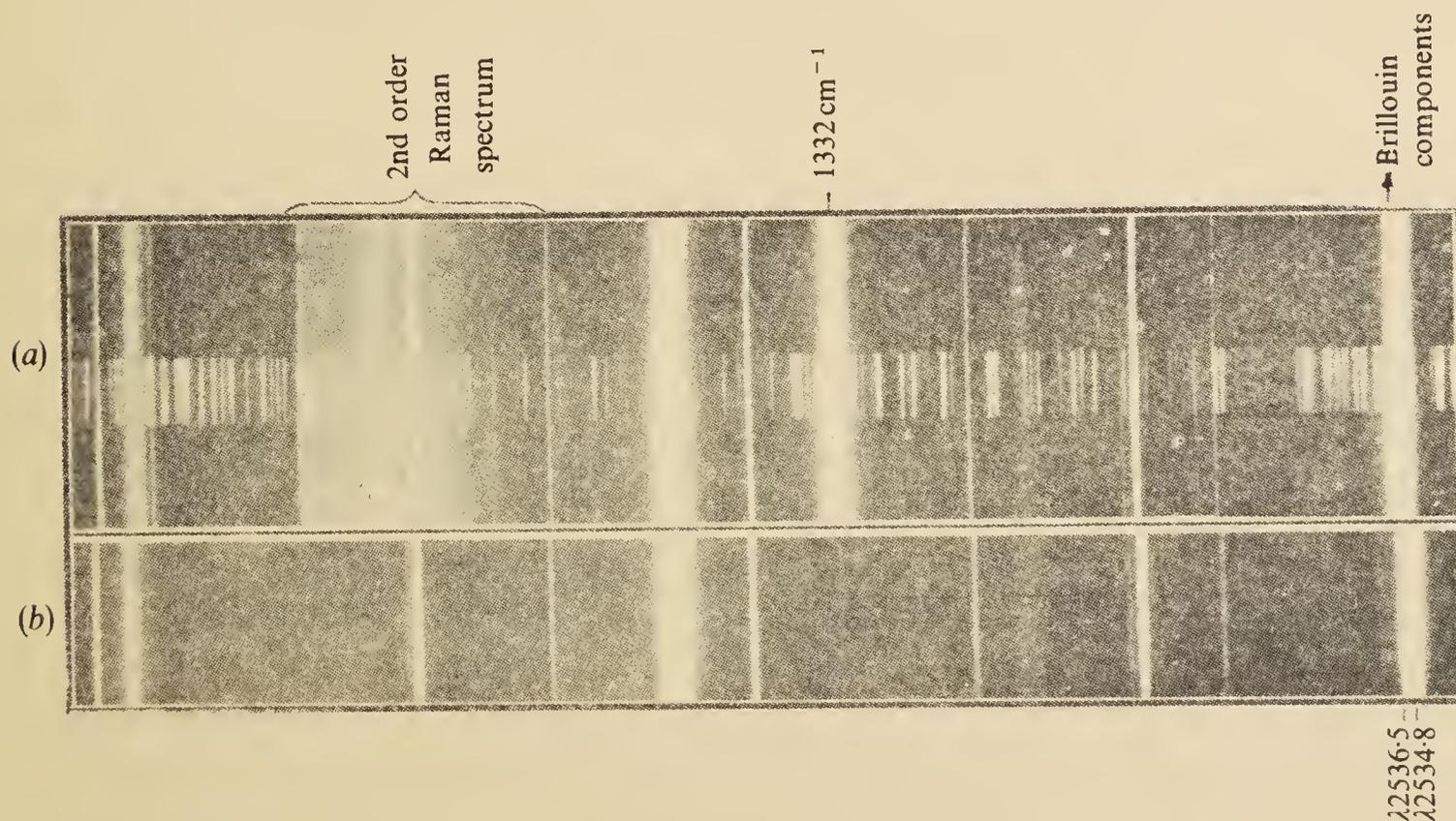


Figure 6. (a) Mercury spectrum. (b) Raman spectrum of diamond (after Dr R S Krishnan).

Brillouin shifts in the vicinity of the exciting radiation λ 2536.5 are less intense than the first-order frequency shift of 1332 cm^{-1} , but both are recorded with short exposures, while the second-order spectrum requires much heavier exposures. Under the high resolution provided by the Hilger E_1 quartz spectrograph, the Brillouin components due to the longitudinal and transverse sound-waves which reflect the light waves are successfully resolved from each other (figure 7), the transverse sound-waves for some unexplained reason giving

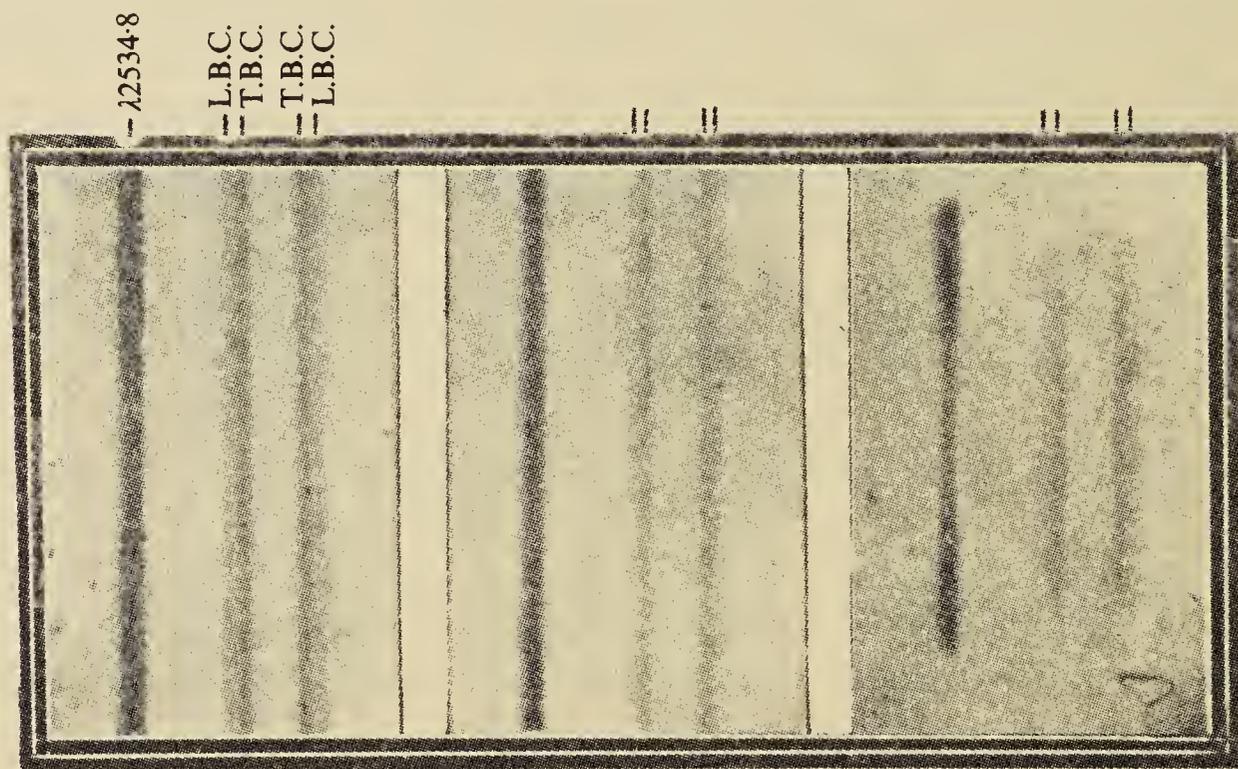


Figure 7. Scattering of light by longitudinal and transverse sound-waves in different directions in diamond (after Dr R S Krishnan).

the more intense components. That sound velocities of both kinds determined from the frequency shifts are found to vary with the direction of their travel [*vide* figures 7(a), (b) and (c)] is to be expected theoretically. Their numerical values for the different directions agree fairly well with those determined by Bhagavantam and Bhimasenachar by the ultrasonic method. The same high-resolution spectrograph also suffices to resolve the spectrum recorded in the region of frequency shifts between 2665.4 cm^{-1} and 2015 cm^{-1} into discrete lines. The shift 2665.4 cm^{-1} which stands out very clearly in the spectrum as a distinct line is clearly the octave of 1332 cm^{-1} . It is much less intense than the close doublet $2460\text{--}2470\text{ cm}^{-1}$, adjacent to which there are also several other lines (see figure 8). The terminal line at 2015 cm^{-1} is so feeble that it is not seen in the reproduced spectra but is quite clearly shown by a microphotometer record. The apparently continuous background seen in the second-order spectrum appears under high resolution as an aggregate of closely spaced lines which is part of the *third-order spectrum* and which appears superposed on it.

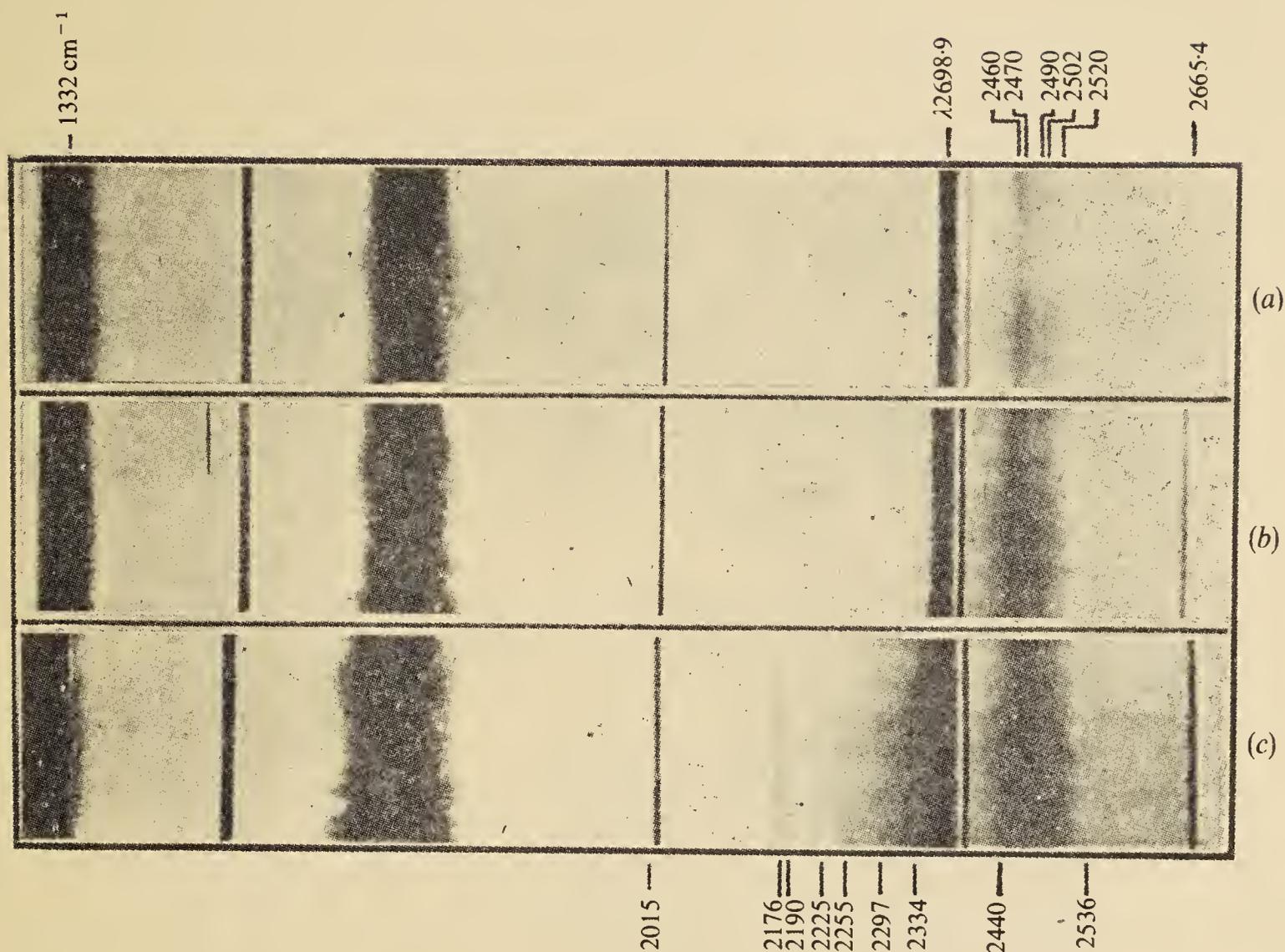


Figure 8. Raman spectrum of diamond under high resolution (after Dr R S Krishnan).

The infra-red absorption by diamond in the frequency range between 900 cm^{-1} and 4000 cm^{-1} has been surveyed by K G Ramanathan and a set of ten curves showing much significant detail obtained with different diamonds is reproduced with his paper. The plates employed were of not very different thicknesses, but they differed much in their physical properties such as ultraviolet transparency, luminescence, birefringence, and photoconductivity. The ten infra-red absorption curves exhibit a practically continuous sequence of variation, ranging from complete transparency in the region $900\text{--}1350\text{ cm}^{-1}$ to nearly complete opacity in the same region, and such variation also shows a complete correlation with the variations of the other properties referred to. With another paper by the same author, the emission and absorption spectra of blue-luminescent diamonds and their microphotometer records are reproduced. The discrete character of the blue-luminescence spectrum is evident from the reproductions (see figure 9), and the measured frequency differences from the principal emission line at $\lambda\ 4152$ indicate very clearly that we are concerned here with the characteristic vibration frequencies of the diamond structure.

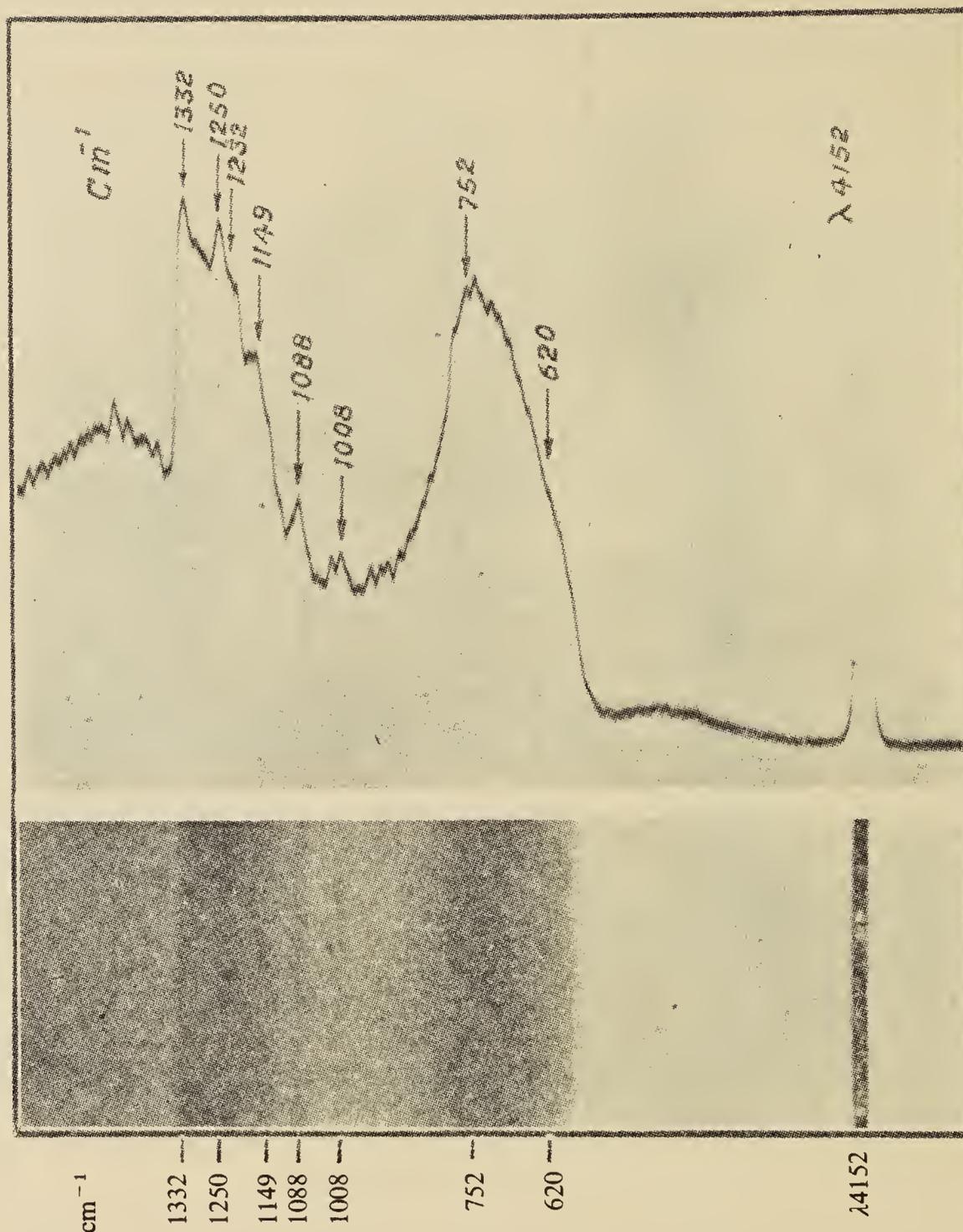


Figure 9. Blue-luminescence spectrum of diamond and its microphotometer record (after K G Ramanathan).

Thus, in the case of diamond, we have a wealth of experimental material regarding the nature of the vibration spectrum obtained by diverse methods of observation, viz., first and second order scattering of light, infra-red absorption of the first and second orders – the former varying from diamond to diamond while the latter remains invariable – luminescence of various types, as also the related absorption. An intercomparison of the results obtained by different methods taking into account the different circumstances of observation, shows a remarkable concordance, which is exhibited diagrammatically in figure 10. The observations themselves clearly indicate that the diamond structure has a set of discrete modes and frequencies of vibration which are finite in number, these appearing in the first-order spectra as fundamentals and in the second-order

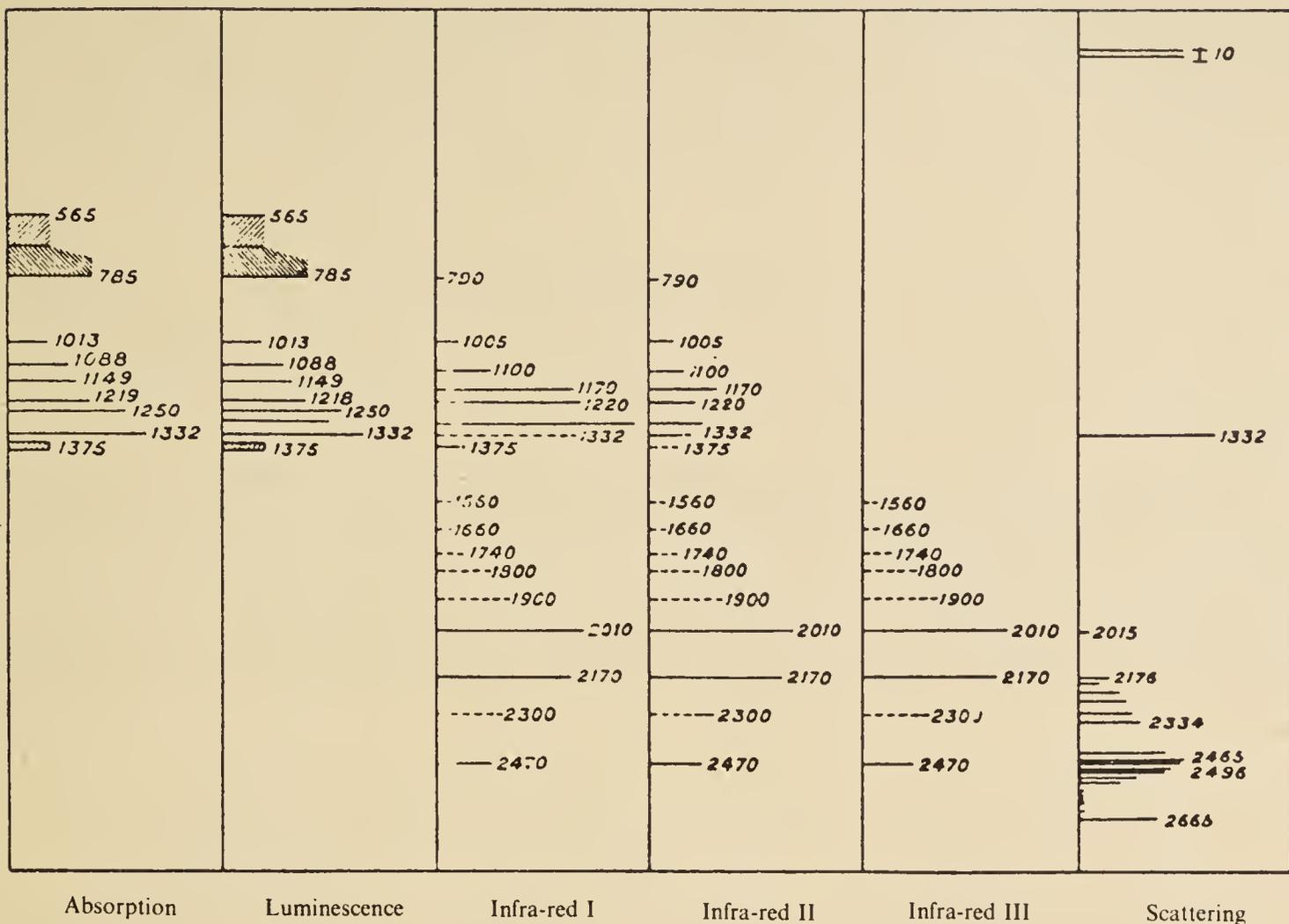


Figure 10. Spectral frequencies of diamond in cm^{-1} as observed by various methods.

spectra as their overtones and summationals. The fundamental frequencies deduced from the observations are in cm^{-1} , 1332, 1250, 1232, 1149, 1088, 1008, 752 and 620, being just 8 in number. The dynamical theory set out in the introductory paper of the symposium leads to the result that the structure of diamond has nine characteristic modes of vibration of which the fifth and the sixth are indistinguishable, thus giving us only eight eigenfrequencies. The identification of these with the eight experimentally observed frequencies therefore naturally suggests itself, but such identification evidently demands an independent proof before it can be accepted as convincing. The two other papers on the case of diamond appearing in the symposium, respectively by the present writer and by Mr K G Ramanathan, furnish the required demonstration.

The nine eigenvibrations of the diamond structure are readily described. Eight of them arise from the existence of three sets of alternative possibilities, namely, an oscillation of the cubic (octahedral) planes in a direction normal (tangential) to those planes, the nearest layers of carbon atoms being in the same (opposite) phase of motion. The ninth mode is a movement of the two sets of carbon atoms forming the structure against each other. Owing to the high symmetry of the structure, the number of independent force-constants required to evaluate the frequency of any one of these modes is very considerably reduced. Actually, three

force-constants (P, Q, R) which express the interactions with the nearest four atoms are sufficient to give a fair approximation to the facts, while eight constants (P, Q, R, S, U, W, Σ , Ω) which take account of the 28 nearest atoms are all that are needed. The values of P, Q, R which fit the experimental data are found to be related to each other in a manner which one would expect from the known physico-chemical structure of diamond (viz., $P > 4Q$ and $2Q > 2R > Q$). The values of the remaining five constants which express the interactions with distant atoms come out very small as is to be theoretically expected. Tables 1 and 2, reproduced from the paper by K G Ramanathan, exhibit this situation very clearly.

The agreement of the frequencies computed theoretically with those observed and the reasonable values of the force-constants which have to be assumed to fit the data are both impressive. But even a more striking confirmation of the correctness of the identifications comes to hand when we consider the *activity* of the various modes in light-scattering and infra-red absorption on the basis of the

Table 1. Numerical values of the force-constants $\times 10^{-5}$ dynes per cm

Atom 0	Atoms 1 to 4		Atoms 5 to 14			Atoms 17 to 28	
P	Q	R	S	U	W	Σ	Ω
7.35	-1.39	-0.858	-0.005	-0.131	-0.114	-0.06	+0.005

Table 2. Calculated value of the frequencies of diamond

Sequence	Degeneracy	Operative force-constant	Frequencies from abbreviated formulae			
			P only	P, Q, R	P, Q, R S, U, W	Complete formula
I	3	$P - 4Q + 4S + 8U - 12\Sigma$	cm^{-1} 1020	cm^{-1} 1 51	cm^{-1} 1294	cm^{-1} 1332
II	8	$P - 2Q - 2R + 4W + 6\Sigma$ $+ 6\Omega$	1020	1294	1269	1250
III	6	$P - 4R - 4S - 12\Omega$	1020	1234	1236	1232
IV	4	$P + 2Q - 4R - 8W - 6\Sigma$ $+ 12\Omega$	1020	1064	1123	1149
V & VI	3 + 3	$P + 4S - 8U$	1020	1020	1088	1088
VII	4	$P - 2Q + 4R - 8W + 6\Sigma$ $- 12\Omega$	1020	973	1038	1008
VIII	6	$P + 4R - 4S + 12\Omega$	1020	744	746	752
IX	8	$P + 2Q + 2R + 4W - 6\Sigma$ $- 6\Omega$	1020	635	582	620

known structure of diamond and compare the same with the facts of observation. This is done at considerable length in the second paper of the symposium, and the concordance which emerges is so satisfying as to leave no doubt whatsoever of the correctness of the theoretical approach made to the problem.

5. The alkali halides

The symposium under review includes papers by Dr R S Krishnan describing and discussing the results of his investigations on the scattering of light in two of the alkali halides, namely, rock-salt and ammonium chloride, which are both cubic crystals. Figure 11(a) and (b) reproduce the spectrum of rock-salt as recorded by him respectively with the larger and small Hilger quartz spectrographs, but enlarged in both cases to the same size. It will be noticed that the

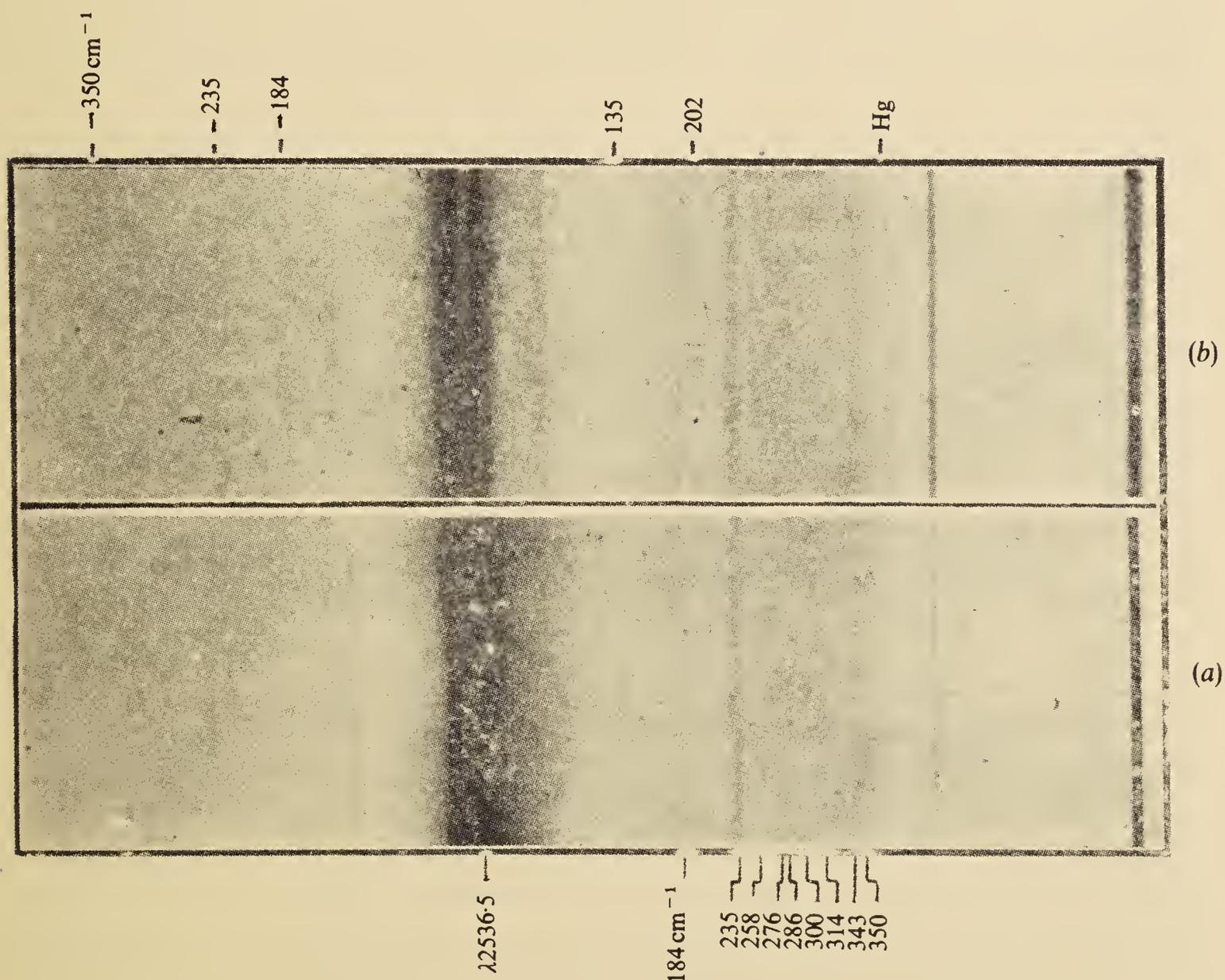


Figure 11. (a), (b) Raman spectrum of rock-salt recorded under high and low resolving powers (after Dr R S Krishnan).

frequency shift of 235 cm^{-1} appears distinctly sharper and that the other details are also seen more clearly in the spectrum recorded with the larger instrument. This is also evident from the microphotometer records reproduced with the paper which show significant differences in the distribution of intensity as recorded with the two instruments. In particular, the frequency shift 235 cm^{-1} shows a large gain in intensity relatively to the other features and indeed overtops all of them in the microphotometer record of the spectrum (see figure 12) which is not the case

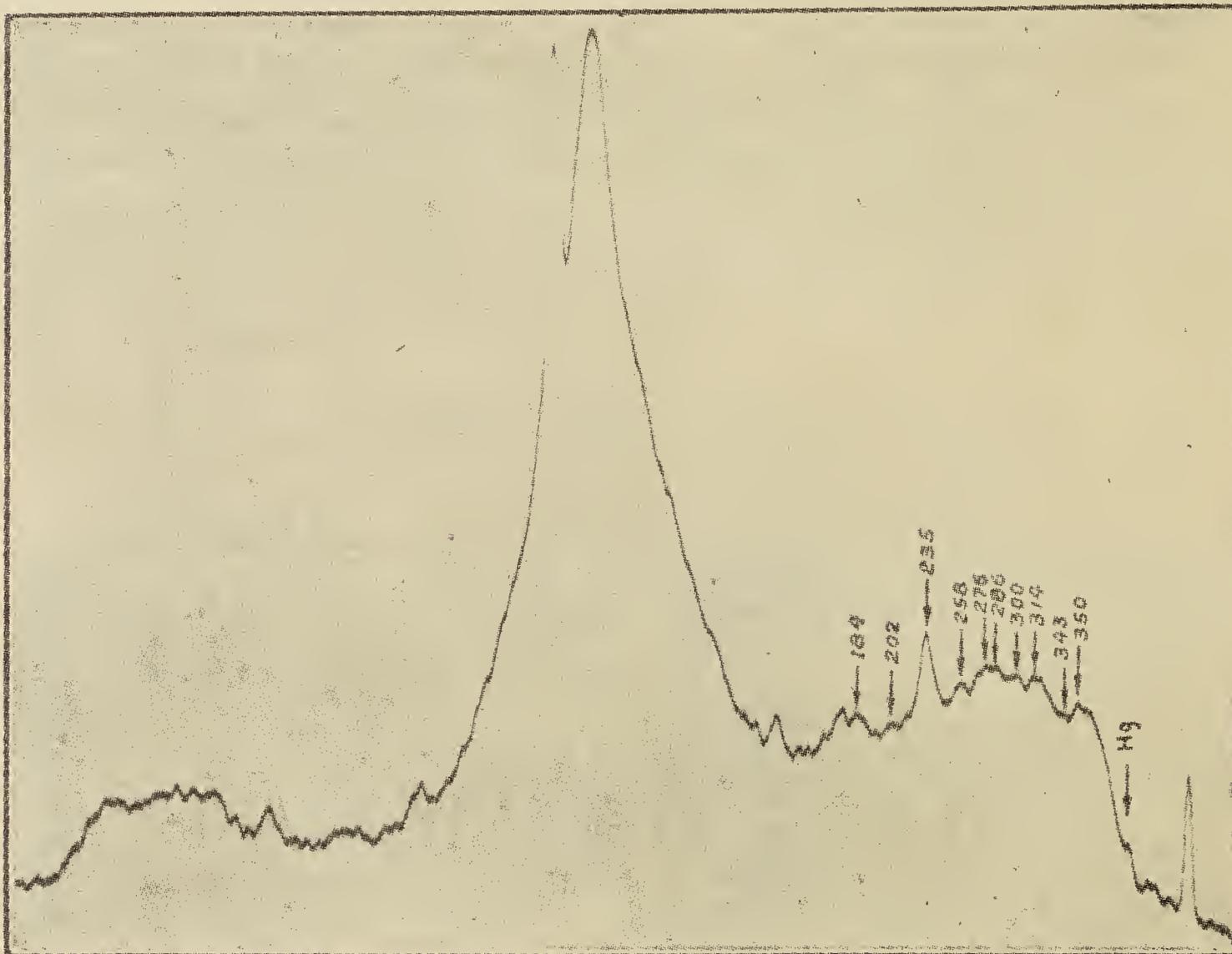


Figure 12. Microphotometer record of the rock-salt spectrum under high resolution (after Dr R S Krishnan).

when the smaller instrument is used. This is precisely what we should expect to find when a higher resolving power is brought to bear upon a closely spaced aggregate to spectral lines of differing intensities. In other words, the comparative microphotometric study reveals that the rock-salt spectrum is an aggregate of discrete lines and that the frequency shift of 235 cm^{-1} shows up a distinct line even under a low resolution just because its intrinsic intensity is much greater than that of the other lines crowded together in the spectrum.

The large intensity with which the frequency shift of 235 cm^{-1} appears finds a simple explanation in the theory of the vibrations of the rock-salt structure developed and discussed in the symposium. One of the nine possible eigen-

vibrations of the structure represents an oscillation of the chlorine ions contained in the octahedral planes of the crystal in a direction normal to these planes, the intervening layers of sodium ions remaining at rest. Owing to the large mass of the chlorine ions, this particular oscillation has a low frequency, being in fact the sixth among the modes in the descending sequence of frequency. The chlorine ions have, however, a large refractivity, indeed very much larger than that of the sodium ions, and hence the alternate approach and recession of the octahedral layers containing them results in much greater variations of optical polarisability than in the case of any other mode. These variations in the successive layers cancel each other's effects in the first approximation, but in the second approximation a residue is left over which results in a frequency shift of double the frequency appearing with quite notable intensity. It is evident from figure 12 that the spectrum also contains numerous other lines, most of which are barely resolved from each other. This is scarcely surprising when we recall that the second-order spectrum of rock-salt should exhibit 45 separate shifts, to say nothing of the third-order spectrum which is also in part superposed on it.

The results obtained with ammonium chloride are also of great interest in view of the remarkable changes which occur in the spectrum of this substance when the temperature is varied. We have, however, no space here to refer to them in detail, and the interested reader will no doubt, consult the original paper.

6. Some concluding remarks

The spectroscopic behaviour of diamond as observed in light-scattering which has been described and discussed above, and the behaviour of crystalline magnesium oxide as observed in infra-red absorption, described and discussed in *Current Science* for December 1947, clearly demonstrate that the complete vibration spectrum of a crystal in the higher ranges of frequency is a discrete *line-spectrum*. In view of the thoroughness with which these two cases have been investigated, and the simplicity of the structure and composition of both the crystals, the experimental facts which have been observed with them are acid tests for any theory which concerns itself with the atomic vibrations in crystals and claims to be able to explain the physical phenomena resulting from such vibrations; any theory which cannot account for the facts noticed with these two crystals or leads to results different from those observed must necessarily stand discredited. *Per contra*, a theoretical approach to the subject which leads to a simple and natural explanation of the facts observed with diamond and magnesium oxide must at least be on the right lines. This is the claim made on behalf of the theory of the eigenvibrations of crystal structures set out and discussed in the introductory paper of the symposium.

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The scattering of light in crystals and the nature of their vibration spectra

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1. Introduction

In an essay¹ by the present writer published in February 1922, it was remarked that transparent crystals, such as ice and quartz, when traversed by an intense beam of white light, exhibit an observable blue opalescence due to the diffusion of the incident radiations by the thermally induced fluctuations of density and refractive index in the medium. Six years later,² the use of monochromatic light and of spectral analysis in such studies revealed that in the radiations scattered by crystals, there are large and readily observable shifts of frequency. The field of investigation opened up in 1922 was thus vastly enlarged by the discovery of 1928. Since that time, many investigations have been made and much valuable knowledge gathered regarding the scattering of light in crystals and the accompanying changes of frequency.

In any attempt to connect the physical properties of crystals with their ultimate structure, we inevitably come up against the following questions. What is the nature of their vibration spectra, and how are the modes and frequencies of vibration of the atoms in a crystal related to its structure? The answers to these questions are of fundamental importance to the physics of the solid state. The study of the spectral shifts observed in light-scattering is the most powerful method available to us for obtaining information concerning these issues. It is the purpose of the present paper to show that a consideration of the facts ascertained by such studies enables us to reach definite conclusions regarding the questions raised above.

2. The two types of light scattering in crystals

Spectroscopic studies have shown that the scattering of light in crystals is of two distinct species which differ fundamentally in their observable characters and which correspond respectively to the two phenomena whose existence was

recognised in 1922 and in 1928. The first type of light-scattering is an effect primarily of thermal origin; the frequency shifts in it vary with the angle of scattering and are so small that they can only be measured with the most powerful instrumental aids at our disposal. Quantitative studies of this type of scattering have shown that it arises from the presence in the crystal of sound-wave patterns of thermal origin which diffract the light-waves traversing it. In other words, the light-scattering of the first kind is a macroscopic phenomenon which can be explained in purely classical fashion. The second type of light-scattering differs from the first in the magnitude of the frequency shifts which are much larger and correspond to wavelengths in the infra-red spectrum. From this and the fact that similar effects are also observed with other states of molecular aggregation, viz., gases, liquids and amorphous solids, we infer that the second type of light-scattering, unlike the first, is a molecular phenomenon which is explicable only on quantum-mechanical principles. This conclusion is confirmed by many other facts of observation and especially by the results of comparative studies made with materials in diverse states of molecular aggregation. Such studies enable us to understand how the state of aggregation influences the observed phenomena and assist us in reaching a correct interpretation of the effects observed with crystals.

3. The elastic vibrations of crystalline solids

The spectral shifts of frequency observed in the scattering of light by gases are of three distinct species and of widely different orders of magnitude which we associate respectively with the three possible kinds of movement of a free molecule, viz., translation, rotation and vibration. Likewise, in the case of crystals, we shall be justified in assuming that the two types of light-scattering actually observed are associated respectively with the two possible kinds of movement of the lattice cells of a crystal, viz., translations and internal vibrations. The translatory movements have no pre-determined frequency of their own whereas the internal vibrations may clearly be expected to possess characteristic frequencies fixed by the structure of the crystal, viz., by the masses and positions of the atoms and the strength of the interatomic forces. It is thus evident that the two classes of movement differ fundamentally in their nature and they have therefore to be considered separately.

The translatory movements of the lattice cells may properly be identified with the displacements of the volume-elements in the crystal contemplated in the classical theory of elastic wave-propagation in solids. The whole of that theory is based on the assumption that a solid may be subdivided into volume elements small enough to justify their being treated as single particles for the evaluation of their kinetic energy and yet large enough for the potential energy of deformation to be evaluated on the same basis as for a solid of macroscopic dimensions. The

assumption is a justifiable approximation, provided the wavelength of the elastic vibration is large compared with the lattice spacings of the crystal and its frequency is small in comparison with the characteristic frequencies of its structure. But as we go down in the scale of wavelengths or go up in the scale of frequencies, we would inevitably reach and pass the limits beyond which these are no longer valid assumptions. It follows that the ideas and methods of the classical theory of elasticity are limited in their application to the movements in the lower ranges of frequency where the elastic displacements may properly be identified with translatory movements of the lattice cells of the crystal, and only infinitesimal alterations in the interatomic distances are involved. The situation is entirely different in the second class of movements, viz., the internal vibrations of the lattice cells which we now proceed to consider.

4. The characteristic vibrations of crystal structures

The vibrations of a free polyatomic molecule and the internal vibrations in the lattice cells of a crystal differ in so far as that in the latter case, the interactions between each unit of the structure and those surrounding it have to be considered. The results of such interaction can be foreseen by considering the simple example of two pendulums of equal length suspended from a common support. The yielding of the support and the consequent coupling of the pendulums results in the system having two different periods of oscillation instead of one; the oscillations of the two pendulums have equal amplitudes in both cases, but their phases are the same in one case and opposite in the other. In a paper published eight years ago in these *Proceedings*,³ the writer gave a formal proof of the following theorem which is the generalised three-dimensional analogue of the theory of coupled oscillators. *In the normal modes of vibration of the structure of a crystal, equivalent atoms in adjacent cells have the same amplitude of vibration, while their phases are either the same or else opposite in successive cells of the lattice along each of its three axes.* An easy verification of this theorem is furnished by considering the effect of giving the crystal a unit displacement along any one of the three axes of the lattice. Such displacement brings the atoms in a cell into the positions previously occupied by the equivalent atoms in an adjacent cell: since the normal mode is a characteristic property of the crystal structure, we should expect it to remain unaltered following the unit translation, and it is readily seen that this is so in all the cases covered by the theorem and *in no others*. In other words, the theorem provides us with a means of completely enumerating the possible normal modes of vibration of the structure of the crystal.

Since the phases of the vibration of equivalent atoms in adjacent cells may be either the same or opposite along each of the three axes of the lattice structure, we have $2 \times 2 \times 2$ or 8 distinct situations regarding the relative phases of the vibrations in a unit cell and in those surrounding it. Thus, when we proceed to

write down the $3p$ equations of motion of the p atoms in a unit cell, taking into account the interactions with the atoms in surrounding cells, we have to consider 8 different sets of $3p$ equations, each of which contains $3p$ variables. Accordingly, we obtain $24p$ solutions in all. This total number may be subdivided as follows: $(3p - 3)$ solutions represent normal modes of vibration in which the phases are the same in adjacent cells of the structure; $21p$ solutions represent normal modes in which the phases of vibration are opposite in adjacent cells along one, two or all three of the axes of the lattice; and finally a residue of 3 solutions which represents the three excluded translations. An element of volume whose dimensions are twice as large and whose content is therefore 8 times as great as for a unit cell of the crystal, would contain $8p$ atoms whose total degrees of freedom would number $24p$. The $(24p - 3)$ normal modes of vibration indicated by the theory may therefore be regarded as the modes of internal vibration of the atoms included in this 8-cell unit, and the 3 excluded solutions as the three translations of such unit.

5. The nature of the vibration spectrum

The results of the two preceding sections may be summed up by the statement that the character of the vibration spectrum is totally different in the two regions of it arising respectively from the translations and vibrations of the lattice cells of the crystal. The translatory movements give us a continuous spectrum of elastic vibrations lying in the lower range of frequencies, while the vibratory movements give us a line-spectrum which is characteristic for the crystal and appears in the upper or infra-red range of frequencies. The total degrees of freedom of atomic movement in the crystal are divided between the two species of vibration in the proportion of $(24p - 3):3$. Thus, even in crystals with the simplest structures for which $p = 1$, only one-eighth of the total degrees of freedom appears as vibrations of the elastic solid type. For crystals with more complex structures for which $p = 2$ or 3 or any larger number, the proportion is correspondingly smaller and the vast majority of the degrees of freedom appear as the characteristic modes of vibration of the crystal structure.

The foregoing results enable us without further explanation to understand the phenomenon exhibited by crystals in light-scattering. It is known that the frequency shifts exhibited by crystals appear, in general, as sharply defined lines. They evidently owe their origin to the activity in light-scattering of one or more of the $(3p - 3)$ characteristic modes of vibration in which the phase is the same in adjacent cells: the remaining $21p$ modes are necessarily inactive, since their vibrations alternate in phase along one or more of the axes of the lattice. The number of frequency shifts actually observed in any case may be fewer than $(3p - 3)$. For, as a consequence of the symmetry properties of the crystal, some of the $(3p - 3)$ modes may have the same frequency and the number of distinct

frequencies would thereby be reduced. Again, some of the $(3p - 3)$ modes might be inactive by reason of their being of an antisymmetric type.

The continuous spectrum of elastic vibrations would necessarily be inactive in light-scattering, since the phase alternates in successive cells of the stationary wave-pattern. An exception, however, arises when the separation between the nodal planes of the pattern is so related to the wavelength of the light traversing the crystal and the angle of incidence on the nodal planes that there is a coherent reflection of the incident light waves by the elastic wave pattern. Such a reflection would exhibit frequency shifts, both positive and negative, the magnitude of which depends on the angle of scattering, as is actually observed.

6. Overtones and combinations

The so-called second-order spectra of light-scattering are very feeble and can only be recorded under intense excitation. They appear when the amplitudes of atomic vibration in any particular mode or modes are finite in comparison with the interatomic distances. For, in such a case, the anharmonicity of the optical polarisability would result in the scattered radiations including spectral components whose frequency shifts are overtones and summations of the vibration frequencies of the modes under consideration.

It is evident that the thermally excited vibrations of the elastic solid type would be incapable of giving any observable second-order effects. For, the energy of any such vibration having a specified frequency would be distributed over the volume of the crystal and the amplitudes of vibration could, therefore, only be infinitesimal. The interatomic displacements associated with the translatory movements would be of a still smaller order of magnitude. Hence, the local variations in optical polarisability associated with the elastic vibration of any particular frequency would be excessively small, and since they vary in phase from point to point within the crystal, their external effects would cancel out completely. In other words, the elastic vibrations of all frequencies are inactive in light-scattering not merely in the first approximation, but absolutely, except in the particular case of a coherent reflection already referred to. Even in this case, there could be a first-order effect but none of higher order.

The situation is altogether different in the case of the characteristic vibrations whose frequencies lie in the infra-red range. The excitation of these vibrations is a quantum-mechanical effect, and the energy of excitation would necessarily be localised in the element of volume under consideration, viz., a group of lattice cells whose linear dimensions are of the same order of magnitude as the range of the intermolecular forces. A quantum of vibrational energy when distributed over such a small volume would result in atomic movements of finite amplitudes and hence, as the result of optical anharmonicity, give rise to scattered radiations with overtones or summational frequency-shifts.

The second-order spectra arising in the manner explained could include overtones and summations of the frequencies of all the $(24p - 3)$ modes and not merely of those modes which are active in the first-order. The $21p$ modes which are inactive in the first approximation may thus become accessible to observation, though only as overtones or summations. The second-order spectrum of light-scattering would necessarily be a line spectrum. But as the overtones and summations would be numerous, it would be a crowded spectrum, and further crowding up may arise from subsidiary effects, such as a splitting up of individual overtones or summations into several distinct components as the result of mechanical anharmonicity and removal of degeneracy. We cannot, therefore, expect the line character of the second-order spectrum to be quite so obvious to inspection in all cases as with the spectrum of the first-order.

7. The theoretical conclusions

We may now sum up the conclusions reached in the preceding sections.

- I. The frequencies of characteristic vibration of the structure of a crystal constitute a line spectrum. This is accompanied by a continuous spectrum of elastic vibrations in the lower ranges of frequency. Only 3 out of every $24p$ degrees of freedom appear in the latter.
- II. The $(3p - 3)$ characteristic modes in which the phase of the vibration is the same in adjoining cells of the structure may appear as frequency shifts in light-scattering; the $21p$ modes in which the phase alternates along one, two or all the three axes of the lattice are inactive.
- III. Overtones and summations of the frequencies of all the $(24p - 3)$ modes are, however, allowed as frequency shifts in light-scattering.
- IV. The continuous spectrum of elastic vibrations is inactive in light-scattering except in the particular case of a coherent reflection of the light-waves by the elastic wave-patterns. Overtones and summations of their frequencies are totally forbidden.

8. Some illustrative examples

(i) *Diamond* (figure 5 in plate III and figures 6 and 7 in plate IV)—The simplicity of the structure of diamond and its cubic symmetry enable its characteristic modes of vibration to be completely described and their frequencies to be evaluated by a rigorous procedure. The $(24p - 3)$ or 45 modes possible give only 8 distinct frequencies. Expressed in wave-numbers, they are, 1332(3), 1250(8), 1232(6), 1149(4), 1088(6), 1008(4), 752(6) and 620(8), the numbers enclosed in brackets being their respective degeneracies. The first or triply degenerate mode represents an oscillation having the same phase in adjacent cells of the lattice,

while the others are modes in which the motion alternates in phase in successive cells. The three elastic constants of diamond can also be computed theoretically from the same set of force-constants as the characteristic vibration-frequencies and used to evaluate the distribution of frequency in the continuous spectrum of elastic vibrations. Thus, all the data necessary are forthcoming for an independent calculation of the specific heats of diamond. A satisfactory agreement is found between the calculated and observed elastic constants, as also between the calculated and observed specific heats over the whole range of temperature for which data are available.

That diamond exhibits a single sharp and intense line with a frequency shift of 1332 cm^{-1} in light-scattering was discovered by C Ramaswamy in the year 1930. More recent investigations by R S Krishnan revealed the second-order spectrum with all the features predicted by the theory. Likewise, it was shown by him that the continuous spectrum of elastic vibrations is completely inactive in light-scattering except in the particular case of a coherent reflection of the incident light-waves by the elastic wave-pattern.

The case of diamond thus affords a complete quantitative verification of the theoretical conclusions set forth above. The reader is referred to recent papers by P S Narayanan⁴ and D Krishnamurti^{5,6} in these *Proceedings* for further details of the case and for literature citations.

(ii) *α-Quartz* [figures 8(a) to (d) in plate V]—The three atoms of silicon and six of oxygen in each unit cell of the structure of quartz give us $(3p - 3)$ or 24 modes of vibration having identical phases in adjoining cells. The trigonal symmetry reduces this number to 16 distinct frequencies and renders 4 of them inactive in light-scattering. Thus, only 12 frequency shifts are to be expected in the first-order spectrum. This is the number actually recorded in moderately exposed spectrograms, provided two rather close doublets actually observed are counted as single lines. If all the $(24p - 3)$ or 213 fundamental frequencies of vibration of the structure could give octaves and summations with observable intensity, the second-order spectrum would obviously be very complex and difficult to decipher. Actually, by giving exposures about a hundred times greater than that necessary to record the first-order spectrum, R S Krishnan⁷ obtained spectrograms which revealed 29 frequency shifts of the second-order. Only 17 of these could be explained as octaves and summations of the $(3p - 3)$ modes, and the remaining 12 therefore presumably represent the strongest amongst the numerous others which are theoretically possible.

(iii) *Calcite and aragonite* [figures 9(a) and (b) in plate V]—Since there are two CaCO_3 groups in each unit cell of the calcite structure, the $(3p - 3)$ characteristic modes of vibration in which the phase is the same in adjacent cells number 27 in all. The trigonal symmetry of the crystal reduces the number of distinct frequencies to 18, of which no less than 13 are inactive in light-scattering, leaving

us with only 5 distinct frequency shifts to be expected in the first-order spectrum. Exposures about 500 times more prolonged than that sufficient to exhibit the first-order frequency shifts enabled R S Krishnan⁸ to record 11 additional frequency shifts which could all be explained as overtones and combinations of the $(3p - 3)$ characteristic frequencies of the structure.

Likewise, in the case of aragonite, R S Krishnan⁹ obtained spectrograms exhibiting 25 frequency-shifts, 19 of which were fundamental frequencies and 6 belonged to the second-order spectrum.

(iv) *Barytes and gypsum* [figures 10(a), (b), (c), (d) in plate VI]—Strongly exposed spectrograms obtained with a large clear block of barytes and a high-speed instrument enabled R S Krishnan¹⁰ to record no fewer than 39 frequency shifts with this crystal. 20 of these which were sufficiently intense to appear on spectrograms obtained with a much slower instrument were interpreted as first-order frequencies, and the remaining 19 (with one exception) as octaves and summations of them.

Likewise, in the case of gypsum¹¹, 34 frequency shifts were recorded of which 29 were identified as belonging to the first-order spectrum and 5 as octaves and summational frequencies.

(v) *The alkali halides* [figures 11(a) and (b) in plate VI]—By reason of the cubic symmetry of the structure of rock-salt, the $(24p - 3)$ or 45 possible modes of its vibration give only 9 distinct frequencies. As each metallic ion is surrounded symmetrically by six halogen ions and *vice-versa*, the triply-degenerate oscillation of the two sets of atoms against each other is inactive and there is, therefore, no first-order spectrum of light-scattering. The total number of octaves and summations which could appear in the second-order spectrum is 45, and since the fundamental frequencies are themselves degenerate in different degrees, mechanical anharmonicity would result in the splitting up of the summational frequencies into several distinct components. Hence, the second-order spectrum of the alkali halides would necessarily be rather complex, and the difficulty of exhibiting its discreteness or line-character would be enhanced by the fact that the entire spectrum falls within a range of 350 wave-numbers in the case of rock-salt and of 300 wave-numbers in the case of potassium bromide. Even so, the fact that some of the lines are much more intense than the rest, e.g., 235 cm^{-1} in the case of rock-salt, makes the true nature of the spectrum evident to inspection, and it becomes even clearer when the spectrograms recorded by R S Krishnan¹² with instruments of lower and higher dispersing powers are compared with each other.

9. Descriptive notes on the spectrograms

The majority of the spectrograms illustrating this paper were obtained by Dr R S Krishnan in the investigations already referred to. A few are by other authors

(T M K Nedungadi, P S Narayanan, M M Patel, V M Padmanabhan and Roop Kishore). All except those in plate I were obtained with the intense excitation provided by the λ 2537 radiations of a water-cooled magnet-controlled mercury arc in quartz. The spectrograms have been reproduced as negatives for the sake of clarity.

Plate I, figures 1 and 2—The spectrograms of naphthalene (crystal), benzophenone (both as liquid and as crystal) and of methyl methacrylate (glass) appearing in these figures illustrate the close similarity of the spectroscopic behaviour of liquids, amorphous solids and crystals in the region of higher frequencies. In all these cases, the larger frequency shifts are seen as sharp lines.

Plate II, figures 3 and 4—This series of six spectrograms illustrates the sharpness of the spectral shifts given with crystals and the increase in their number with increasing complexity of crystal structure. Fluorite gives only one frequency shift, while alumina gives 7, beryllium silicate 25, topaz 32, Rochelle-salt 49, and cane-sugar 63 distinct frequency shifts. The mercury lines have been marked off with the symbol λ in the spectrograms to distinguish them from the frequency shifts given by the crystal.

Plate III, figure 5 and plate IV, figures 6 and 7—These illustrate the case of diamond. The development of a second-order spectrum in the region of frequency shifts between 2666 and 2176 with increasing exposures and its absence in the region of the elastic wave-spectrum even in heavily exposed spectrograms will be seen from figures 5(a), (b) and (c). The microphotometer record in figure 6 and the high-resolution spectrograms in figure 7 exhibit very clearly the sharp lines with frequency shifts 2666, 2460–70 and 2176 which are the octaves of the fundamental frequencies 1332, 1232 and 1088 respectively.

Plate IV, figure 8—This series of four spectrograms illustrates the development of the second-order spectrum of quartz with increasing exposures.

Plate V, figures 9(a) and (b)—These illustrate respectively the spectra of aragonite and calcite which are seen to be strikingly different. Some of the sharply defined lines appearing in the second-order spectrum of calcite are marked in figure 9(b).

Plate VI, figures 10(c) and (d)—These illustrate strongly exposed spectra of barytes. Its second-order spectrum is clearly seen in both figures, but better in the more heavily exposed spectrogram.

Plate VII, figures 11(a) and (b)—Note the sharply-defined line with a frequency shift 235 seen in the second-order spectrum of rock-salt and the intense line with the frequency shift 126 in that of potassium bromide.

10. Summary

The facts of light-scattering in crystals are reviewed and the nature of the atomic movements and the character of their vibration spectra in the different frequency regions are deduced therefrom. Whereas the movements based on the translations of the lattice cells result in elastic wave motions in the solid with a continuous frequency spectrum, the modes based on their internal vibrations are localised and have monochromatic frequencies analogous to those of polyatomic molecules. The total degrees of atomic freedom are shared between the latter and the former in the ratio $(24p - 3):3$. The frequency shifts ordinarily observed in light-scattering arise from the group of $(3p - 3)$ modes in which the phase of the vibration is the same in adjacent cells of the lattice. But these as well as the $21p$ additional modes in which the phase alternates along the axes can give rise to shifts which are overtones and summations of their fundamental frequencies. The localisation of the internal vibrations permits of these overtones and summations appearing as frequency shifts with observable intensity. On the other hand, the continuous spectrum of elastic vibrations is completely inactive in light-scattering, apart from the particular case of a coherent reflection of the light waves by the elastic wave pattern.

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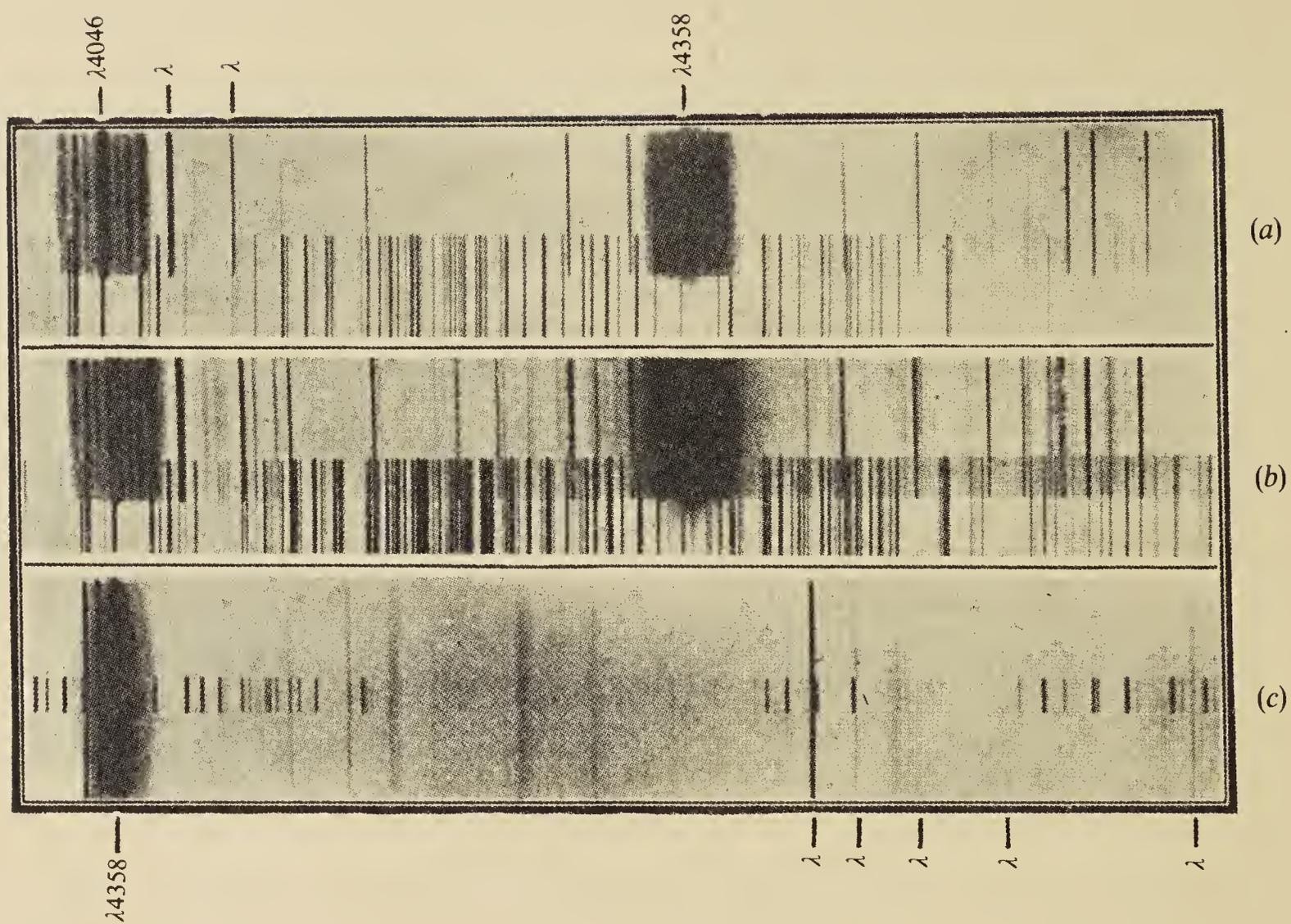


Figure 1. (a) and (b) Naphthalene crystals, (c) Methyl methacrylate glass.

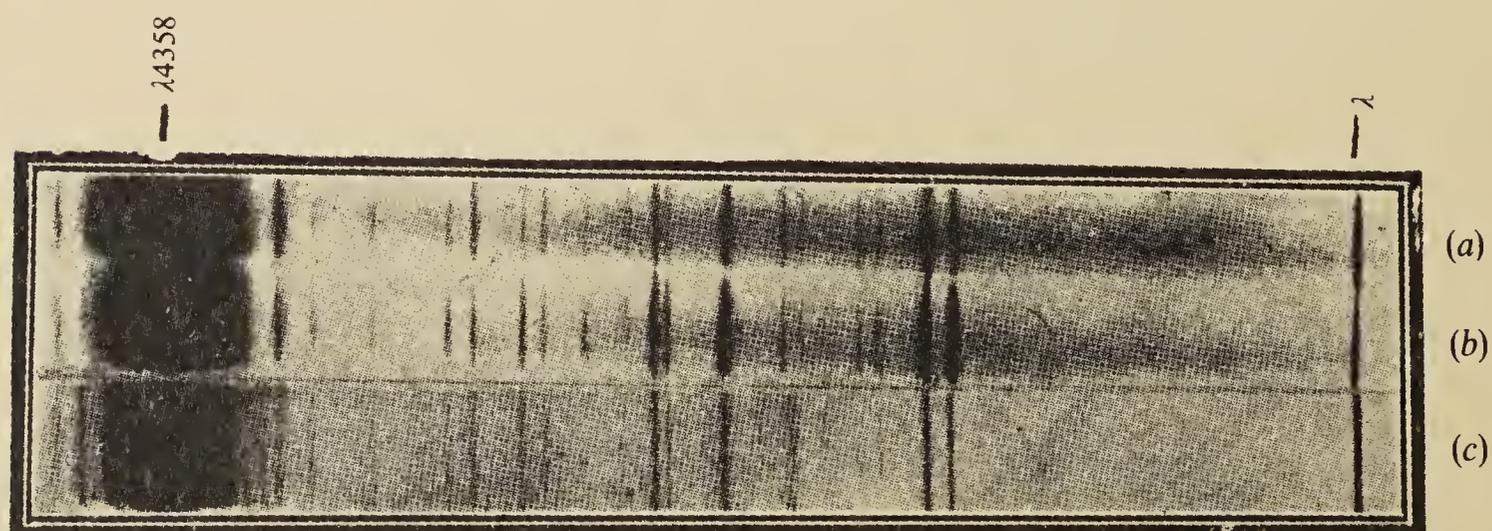


Figure 2. (a) and (b) Benzophenone liquid, (c) Benzophenone crystal.

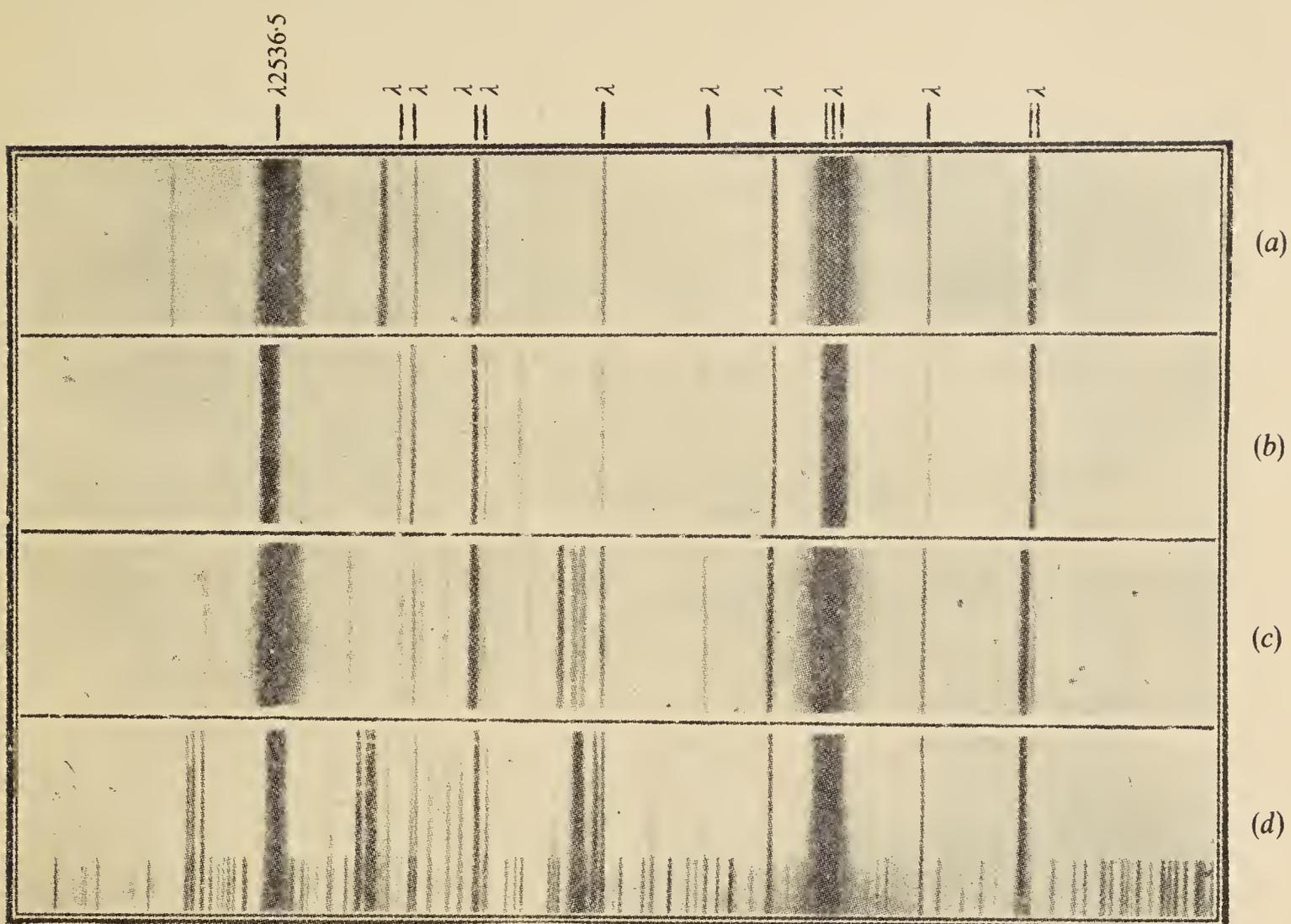


Figure 3. (a) Fluorite, (b) alumina, (c) beryllium silicate, (d) topaz.

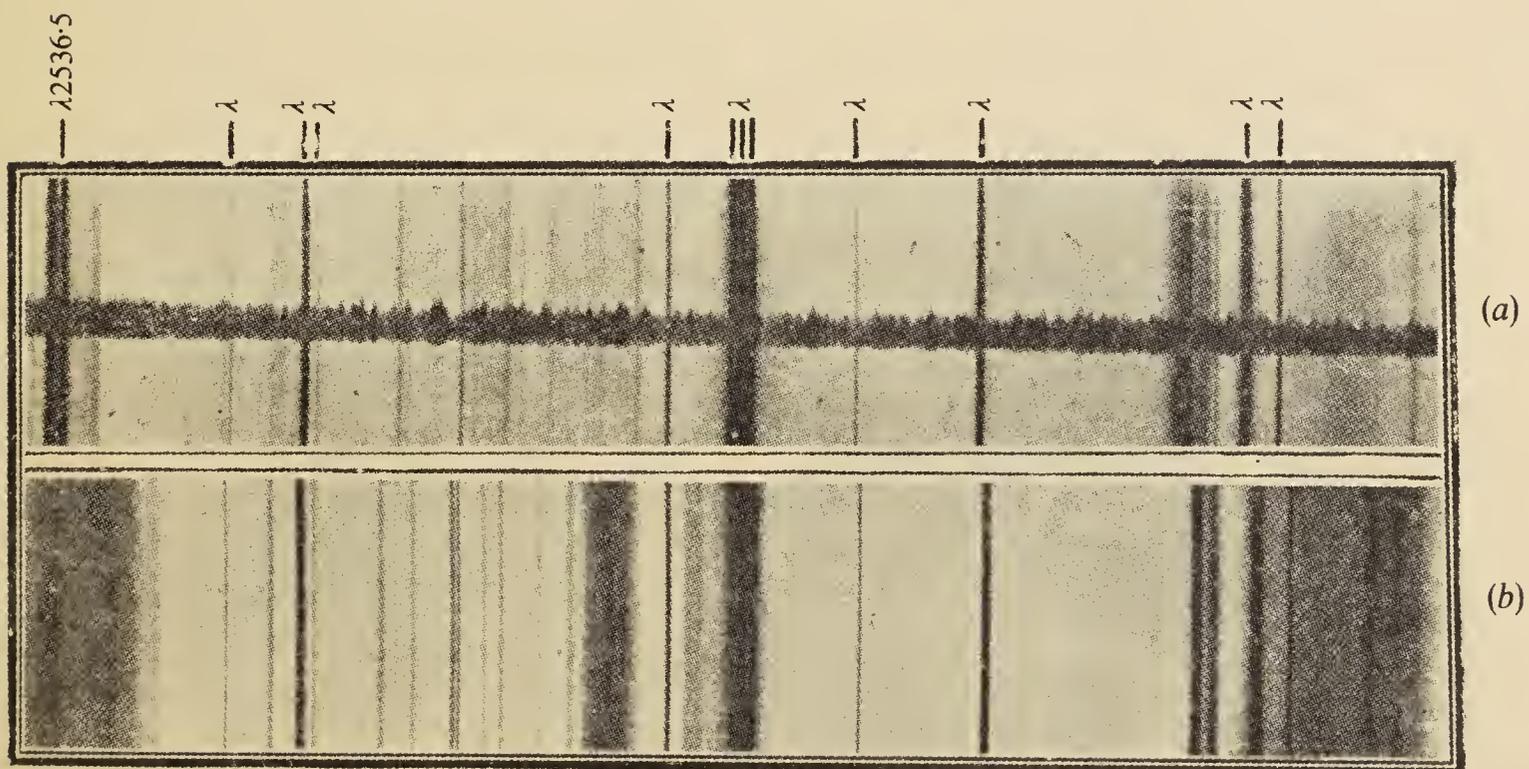


Figure 4. (a) Cane-sugar, (b) Rochelle salt.

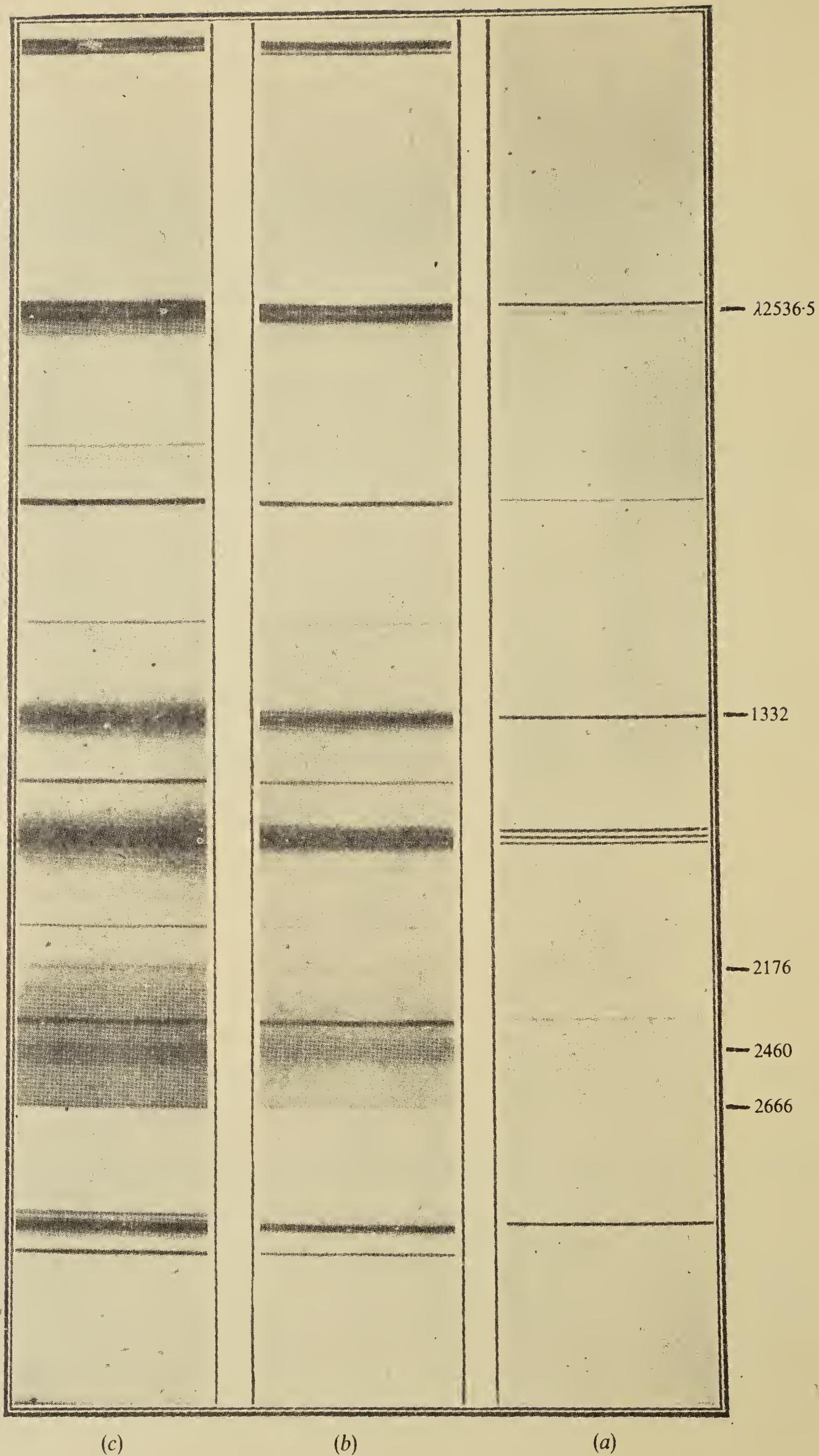


Figure 5. Diamond (medium spectrograph): (a), (b), (c) with increasing exposures.

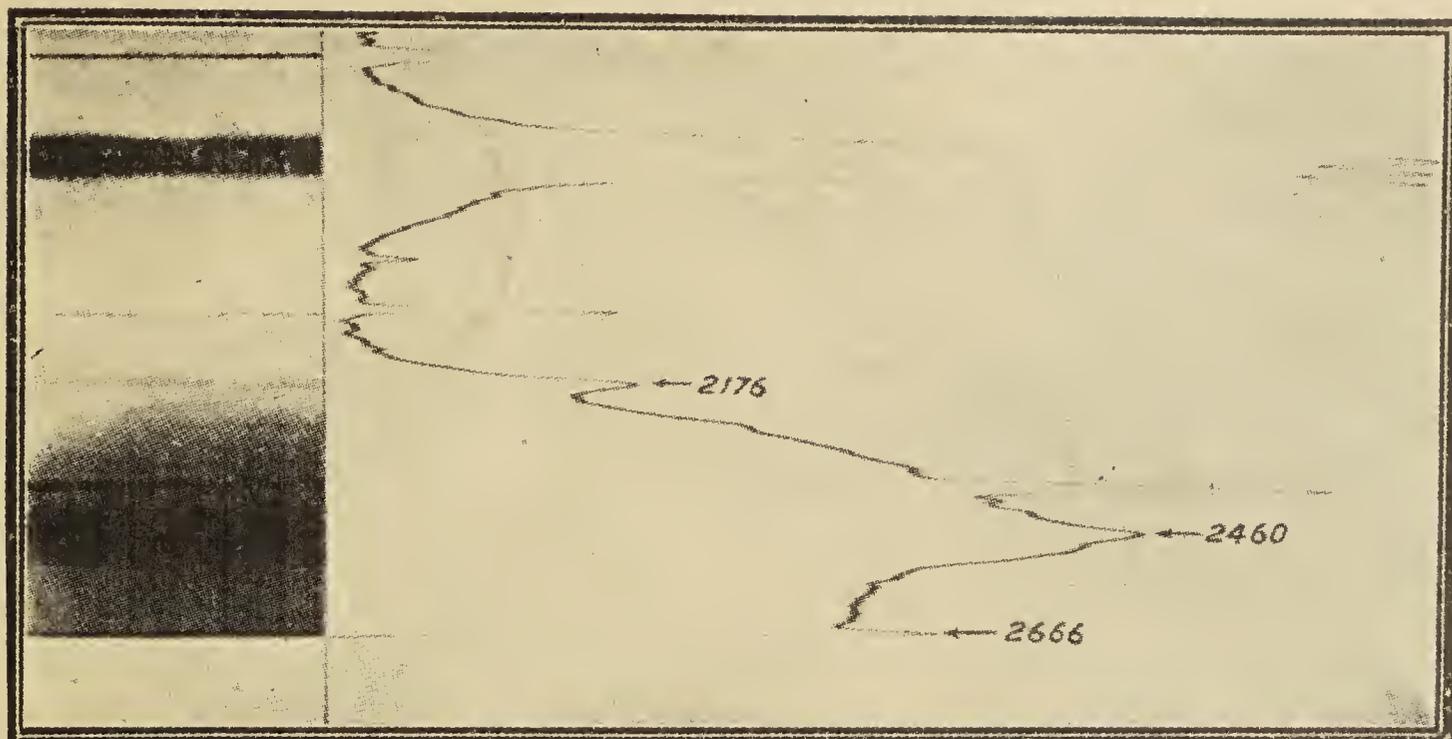


Figure 6. Diamond (medium spectrograph).

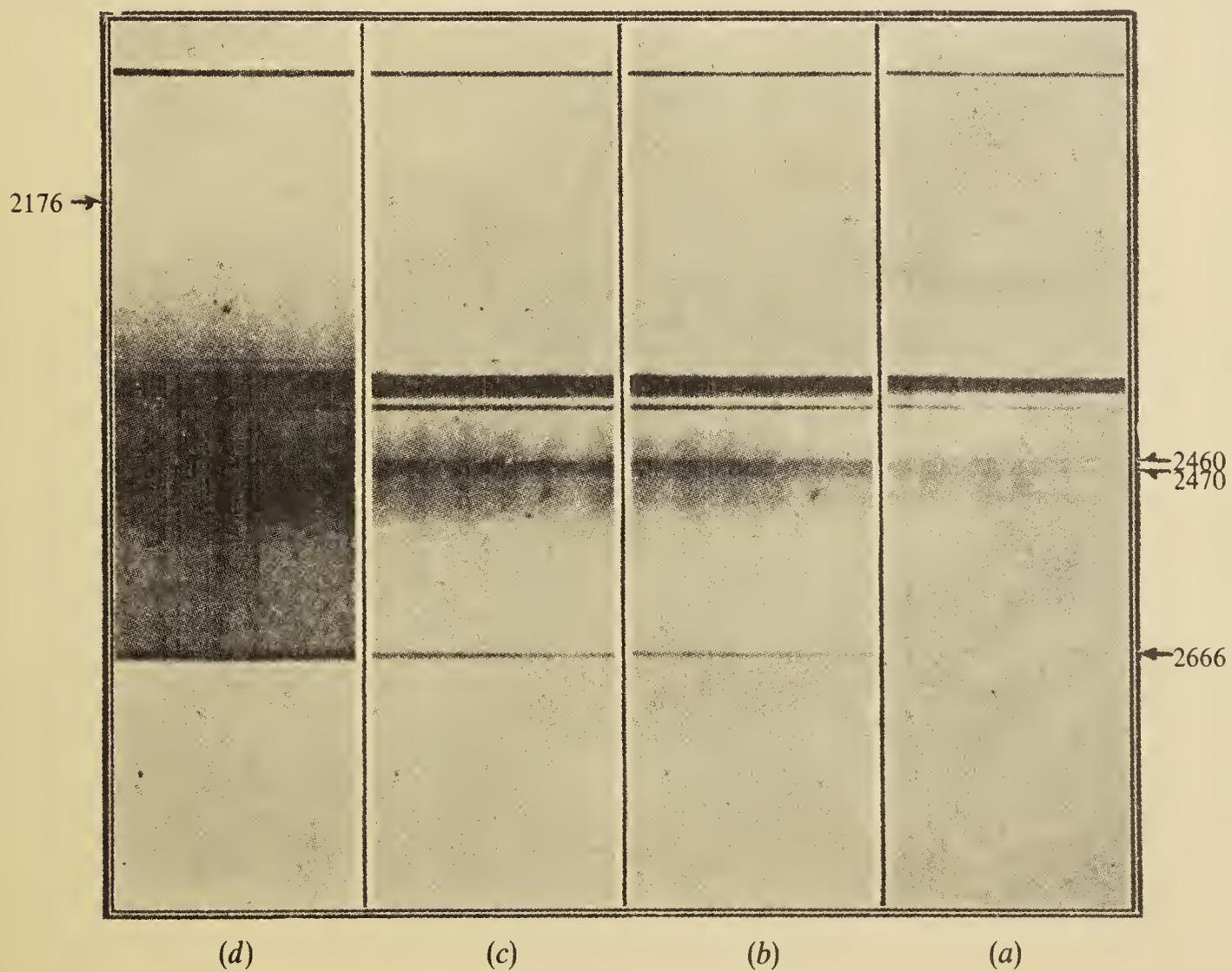
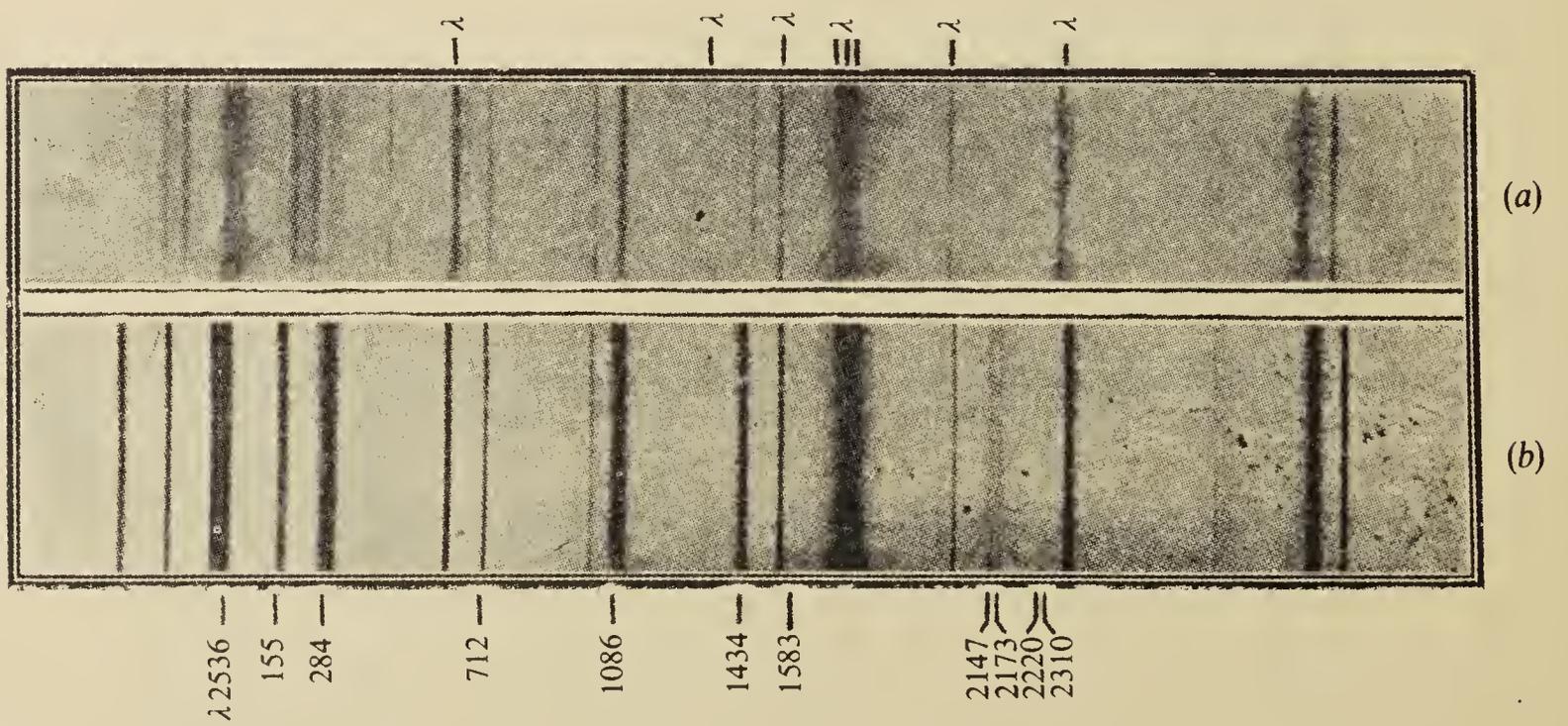
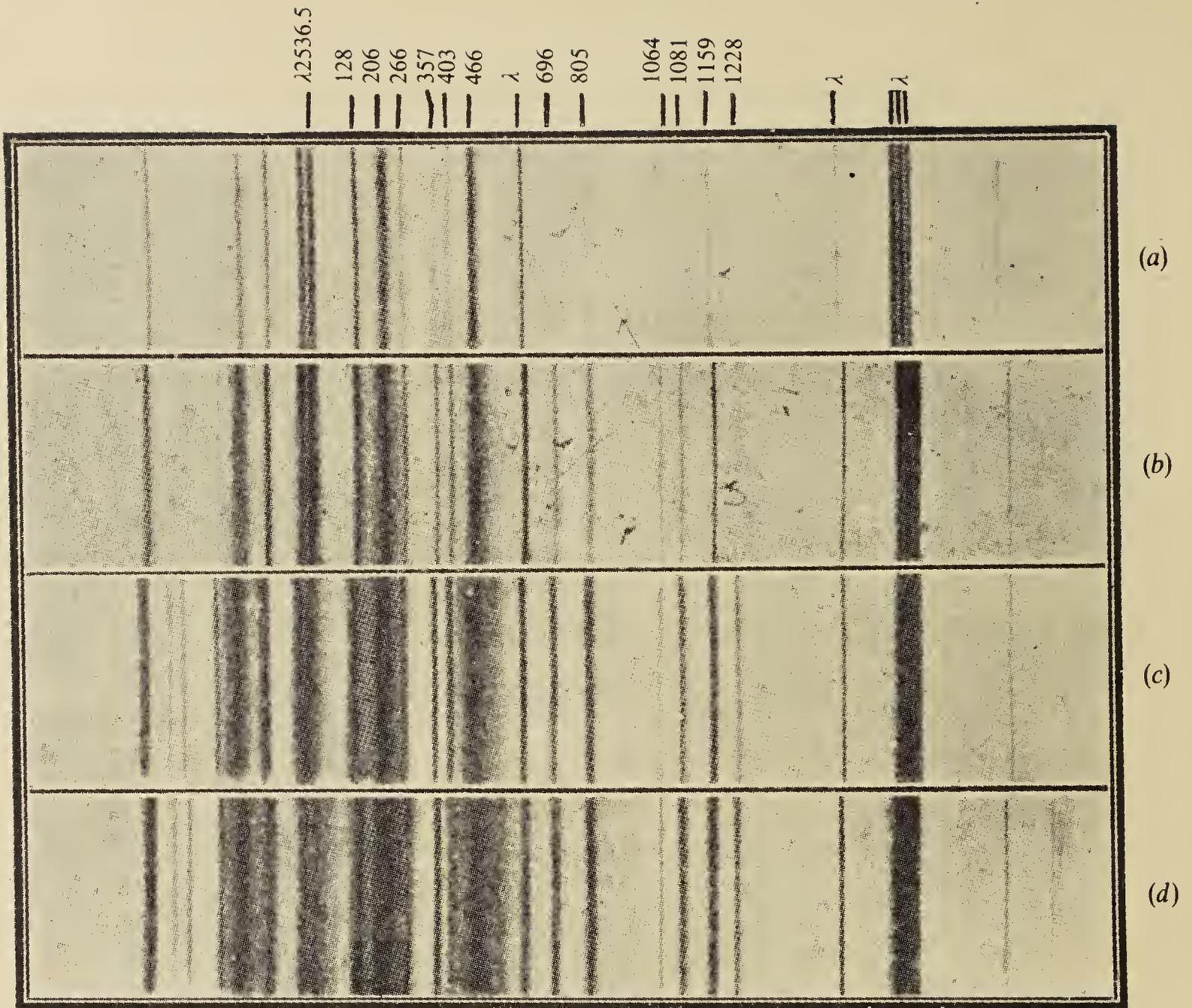


Figure 7. Diamond (large spectrograph): (a), (b), (c), (d) with increasing exposures.



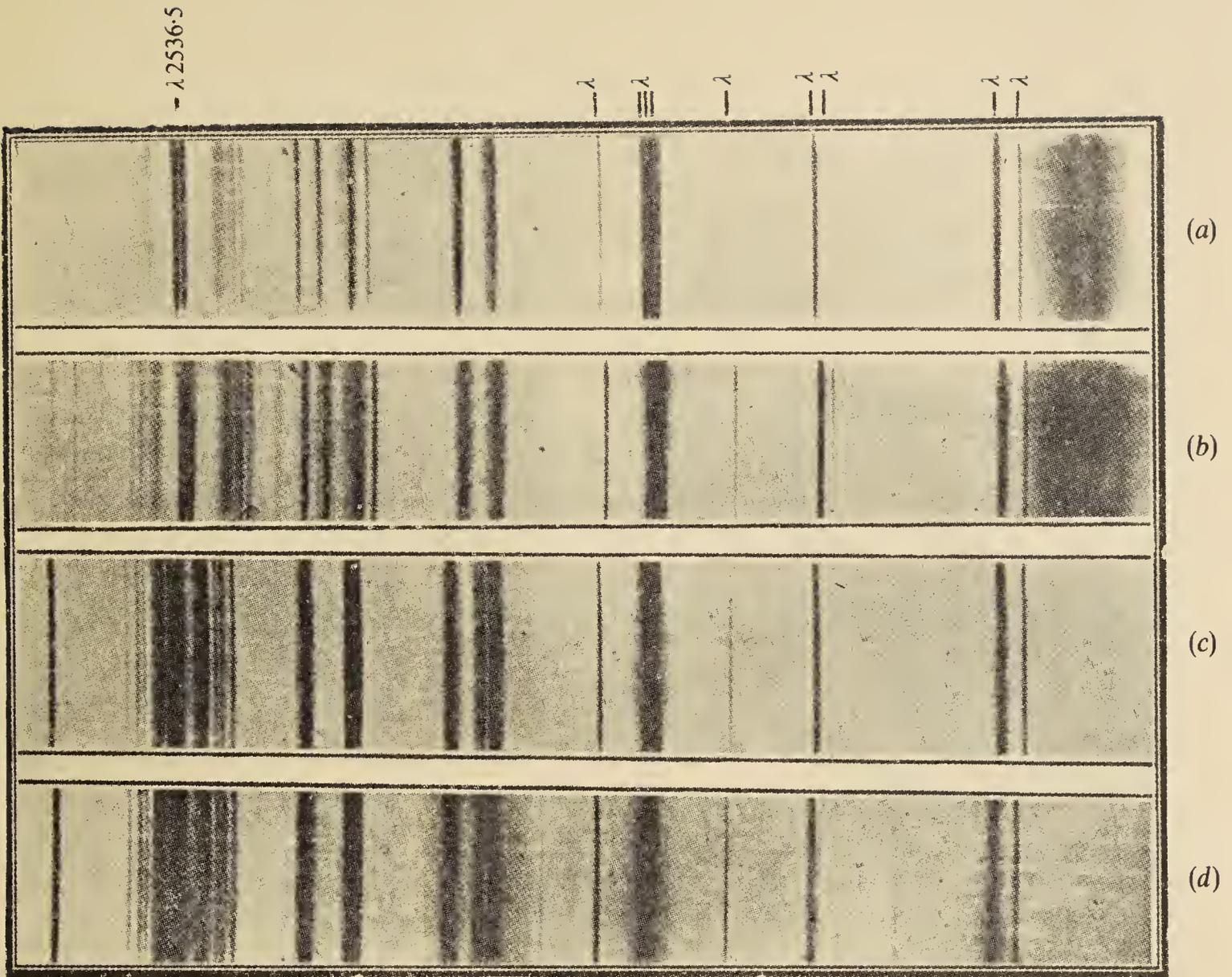


Figure 10. (a) and (b) Gypsum, (c) and (d) barytes, with two different exposures in each case.

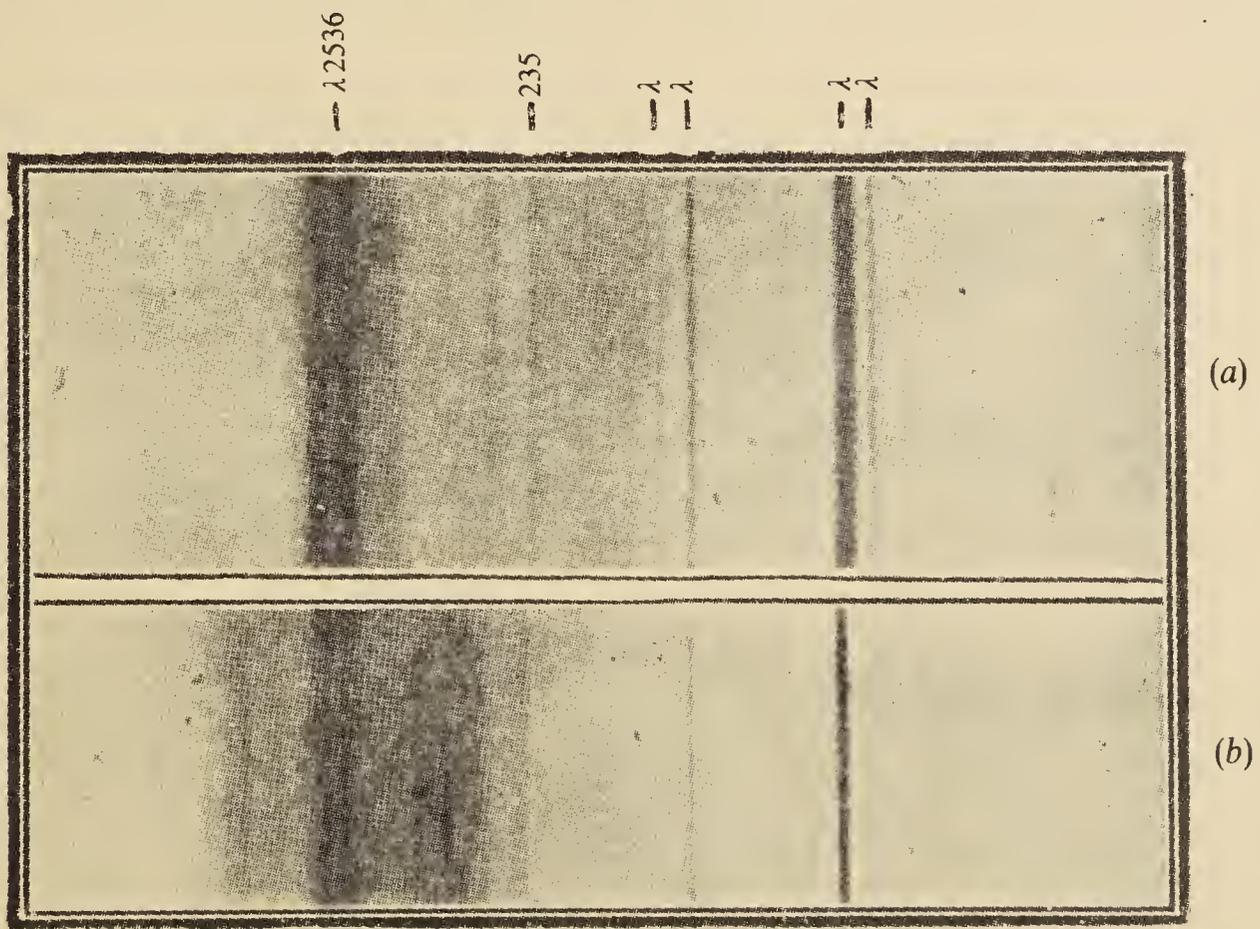


Figure 11. (a) Rock-salt, (b) potassium bromide.

The vibration spectra of crystals and the theory of their specific heats

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1. Introduction

The thermal energy of a crystalline solid may properly be identified with the energy of vibration of the atoms in it about their positions of equilibrium. The theorem in classical mechanics due to Lagrange¹ which states that a connected system of N particles has $3N$ normal modes of vibration enables us to go further and identify the thermal energy with the sum of the energies of these $3N$ vibrations, each having its own appropriate frequency. The problem thus reduces itself to that of determining the distribution in frequency of the $3N$ vibrations. When this is known, we have only to sum up the expressions for the average energies of the individual vibrations given by Einstein's fundamental theorem² to obtain the thermal energy content of the solid at any given temperature.

In the well known theories of the specific heat of solids due respectively to Debye³ and to Born and Karman,⁴ the frequency distribution is found on the basis of certain special assumptions. Following a suggestion due originally to J H Jeans,⁵ these authors identify the $3N$ vibrations with $3N$ different wave-patterns filling the volume of the crystal. The $3N$ different frequencies which result from these assumptions make the vibration spectrum of the crystal a diffuse continuum. Lagrange's theorem, however, does not require that a system of N connected particles should necessarily possess $3N$ *different* frequencies. Indeed, since a crystal is an assemblage of an immense number of similar groups of particles, we should expect that they would all possess identical frequencies of internal vibration. The recognition of this led the present writer to make a fresh approach to the problem in a paper⁶ which was published in these *Proceedings* eight years ago. The results of that paper furnished a simple and forthright explanation of the nature of the vibration spectra of crystals as revealed by the frequency shifts in the scattering of light by them. The theory also indicated some new and previously unsuspected features of these vibration spectra which appeared not inaccessible to observation. Experimental investigations undertaken to test the predictions of the theory have confirmed their reality. In a recent paper by the writer⁷ published in these *Proceedings*, the whole of the work in this

field has been reviewed and it has been shown that the behaviour of crystals in light-scattering completely substantiates the correctness of the approach to the subject made in the paper of 1943.

The present paper is a survey of the theoretical aspects of the subject, while the one just referred to dealt with it from the phenomenological standpoint. Its main purpose is to make it clear that the treatment of the theoretical problem given in 1943 was not only on the right lines but was also a complete and rigorous solution of it. The present paper contains also a critical examination of the premises on which the earlier theories of the subject were based. The identification of the normal modes of vibration of the atoms in a crystal with an immense number of wave-patterns comprised in its volume is shown to be an unjustifiable and wholly misconceived hypothesis. It is also shown that the consequences of that hypothesis are contradicted by the facts of observation.

2. Molecular vibrations in crystals

We shall commence by considering a simple case which approximates to the actual situation in many crystals and assume that an immense number of molecules, all of the same kind, come together and are held in a regular three-dimensional array by forces which are very weak in comparison with the forces binding the atoms together in each molecule. A substance of this kind would have a low melting point and would sublime very readily. We may cite naphthalene as an example. The molecules of the substance in the state of vapour would move, rotate and vibrate independently of each other. In the crystalline state, their translations could no longer be independent. The free rotations would also be suppressed and replaced by periodic angular oscillations. We shall at first consider here only the internal oscillations of the molecules. In the free state, the modes and frequencies of such internal oscillations would be determined by the geometric form of the molecule, the masses of the atoms comprised in it and the forces holding them together. We may ask ourselves, what would be the situation concerning these vibrations in the crystalline state?

Since by assumption, the intermolecular forces in the crystal are very weak, they could scarcely have any effect on either the modes or the frequencies of molecular vibration. The interactions, however, would have an important consequence, viz., that if any one molecule within the crystal is set in vibration, its energy would leak away to the other molecules surrounding it, and from these again to other molecules further out, and so forth, so that ultimately the energy would be dissipated through the crystal. The transfer of energy envisaged would be the slower, the weaker the intermolecular forces are, and would take a very long time before it reaches the external boundary of the crystal. It is thus evident that we are here concerned with a diffusion process and not one of wave-

propagation. From the assumptions made, it follows that the vibration spectrum of the entire crystal in the frequency region under consideration would differ but little from that of the molecules of which it is composed. In other words, it would exhibit a finite number of monochromatic frequencies.

3. The effect of coupling on the molecular vibrations

We may now remove the restriction which we laid upon ourselves for the sake of simplicity, viz., that the intermolecular forces were extremely weak. One effect of an increase of their strength would be to speed up the process of diffusion of the energy of vibration from an excited molecule to those surrounding it. Other important effects have also to be considered, viz., an increase in the frequency of the translational-*cum*-rotational oscillations of the molecules about their positions of equilibrium. The coupling between each molecule and its neighbours would also multiply the number of possible modes of their internal vibrations and alter their frequencies.

The problem which here arises was dealt with and solved in the paper of 1943 quoted in the introduction. Every normal mode must satisfy two conditions, viz., that the particles must all vibrate with the same frequency and that their phases must all be the same or opposite. A third condition is set by the nature of the problem in the case of a crystal, viz., that a normal mode should remain a normal mode, following a unit translation of the crystal along any one of the three axes of the lattice. These three conditions taken together completely determine the possible modes of vibration of the structure of the crystal. There are only two possibilities in respect of the phases of vibration in successive cells of the structure along each axis, viz., that they are the same or else alternate. Thus, in all, there are $2 \times 2 \times 2$ alternative possibilities and therefore eight species of normal modes. The $3p$ equations of motion of the p atoms in the unit cell of the structure would necessarily be different in each species. Thus we have $8 \times 3p$ or $24p$ equations of motion and the same number of solutions. Only $(24p - 3)$ solutions would represent actual vibrations, while the 3 excluded solutions would represent simple translations.

Thus, when the finiteness of the intermolecular forces is taken into account, the structure of the crystal has $(24p - 3)$ modes of vibration, each with its appropriate monochromatic frequency. These would include the translational-*cum*-rotational oscillations of the molecules which are possible by reason of their being held in a regular three-dimensional array. If we imagine the strength of the intermolecular forces to be gradually reduced, the frequency of such oscillations would diminish steadily, while the frequencies of the vibrational modes which are multiplied 8-fold in number by the coupling would converge towards the vibrational frequencies of the molecules in the free state.

4. The enumeration of wave-patterns

We turn now to the examination of the premises on which the specific heat theories of Debye and Born–Karman are based. The enumeration according to frequency or wavelength of the stationary wave-patterns within an enclosure is effected, following Rayleigh,⁸ by assuming for the latter a cubical shape, and counting up the terms of a three-dimensional Fourier expansion which individually are solutions of the wave-equation valid inside the enclosure. It is essential for the argument that the waves travel freely within the enclosed space and are not subject to damping. The slightest damping of the wave during their progression would invalidate the entire procedure. We have, in fact, only to assume that the enclosure is large enough; the waves, if damped, would die away before they could traverse it from end to end and return to build up a stationary interference pattern. On the other hand, wave-propagation in material media is necessarily damped to an extent determined by the physical state of the medium and the wavelength or frequency of the vibration. Indeed, it may well happen that such damping is so enormous as altogether to preclude the possibility of wave-propagation through the medium. Hence, it follows that the identification of the normal modes of atomic vibration within material bodies with stationary wave-patterns determined by the external boundary conditions is a wholly misconceived and erroneous hypothesis.

We may illustrate the foregoing remarks by two typical examples. In the paper already cited, and again later in his book,⁹ J H Jeans put forward a mathematical argument based on the Fourier analysis which claims to prove that the energy of the translatory motion of the molecules in a gas can be identified with the energy of an appropriately chosen number of sound-wave trains in it, the great majority of them having wavelengths of the same order of magnitude as the mean distance between neighbouring molecules. The proof is, however, illusory, since it overlooks the fact that sound-waves in gases are damped by viscosity. No wave-propagation is possible in a gas if the wavelength is as small as the molecular mean free path, and this is itself many times larger than the average distance between neighbouring molecules. In other words, the sound-waves proposed to be enumerated by Jeans have no physical existence!

The second example which we shall consider is that already dealt with in section 2 above. It is evident that a crystal consisting of discrete molecules having their own characteristic frequencies of vibration would present an impenetrable obstacle to the entry and propagation through the substance of “waves” having those self-same frequencies. We have only to recall in this connection the optical behaviour of a cell containing the vapour of sodium or of mercury towards the entry into it of the resonance radiations from a sodium vapour or a mercury vapour lamp respectively, or the behaviour of a rock-salt crystal towards the entry into it of infra-red radiations previously monochromatised by successive reflections at the surfaces of crystals of the same substance. Since the waves

cannot even enter the medium, it would be clearly be a fantastic procedure to identify the molecular vibrations with wave-patterns enumerated on the basis of their free propagation inside the crystal.

5. Wave propagation in periodic structures

The title of this section is the same as that of a book¹⁰ by L Brillouin which was published a few years ago, having the sub-title "Electric filters and crystal lattices". The greater part of that book is devoted to an exposition of the ideas underlying the Debye and Born-Karman theories of crystal behaviour, and it is therefore appropriate that some reference is made to it here. Surprisingly enough, though the book concerns itself with the problem of finding the frequency spectra of crystals, one searches its pages in vain for any reference to the normal modes of vibration of the atoms in a crystal. It would seem, in fact, that Brillouin considers "waves" and "normal modes" as equivalent expressions. This is clearly a misconception. While the fundamental theorem of Lagrange enables us to enumerate the normal modes of vibration of a system, a "wave" is not a normal mode since the phase of the motion in it changes from point to point and from instant and instant, and hence one cannot, in general, enumerate waves. Only when there is perfectly undamped wave-propagation within a perfectly reflecting enclosure does the restriction of the permitted wavelengths to a specifiable but infinite sequence of values resulting therefrom enable us to regard the stationary wave-patterns as equivalent to normal modes. But as already pointed out in the preceding section, there can be no undamped wave-propagation in any material substance consisting of atoms and molecules. It follows that the contents of Brillouin's book are without significance in relation to the problems of crystal physics which it professes to deal with.

The behaviour of macroscopic systems exhibiting some sort of periodicity in their structure, e.g., a stretched string loaded at regular intervals with masses of the same or different kinds, is the theme with which most expositions of the Born-Karman theory commence. It is, therefore, necessary to examine the question whether the behaviour of crystals can at all be compared with those of mechanical models, and if so, with what limitations.

Three basic facts about crystals which we can never hope to reproduce in any artificially constructed mechanical model are, *firstly*, the immense numbers of individual particles constituting even the smallest of crystals: *secondly*, the possibility of independent movement of the atoms and molecules which reveals itself in various ways, and *thirdly*, the high frequencies of vibration which lie mostly far above the limits of validity of the classical mechanics. Besides these vital differences, it should also be pointed out that no macroscopic model can claim to represent the behaviour of a crystal unless it satisfies the conditions requisite for dynamic similarity. In other words, the linear dimensions, masses

and operative forces in the model should be so proportioned to those of the crystal that the actions taking place in the latter are reproduced in the former. If such a model were constructed—even if it be only on paper—it would immediately make it evident that its behaviour, far from supporting the Born lattice dynamics, would show its basic assumptions to be untenable.

6. Mechanical models of crystal behaviour

We shall illustrate the foregoing remarks by considering a model of a diamond crystal, enlarged in its linear dimensions by a factor of 10^7 so that the individual atoms can be conveniently observed, and slowed down in the time-rate of its actions by a factor of 10^{12} so that the movements of the atoms can be visually followed. In the actual crystal, assumed to be 1.54 millimetre in diameter, the highest characteristic frequency of atomic vibration is 1332 cm^{-1} in spectroscopic units, while the highest sound velocity is 18,000 metres per second. In the model which is 15.4 kilometres in diameter, the characteristic frequency is slowed down to 40 vibrations per second, while the fastest sound wave would take 24 hours to travel from the centre of the model to its surface and return again after reflection to the centre. Let us now suppose that a group of atoms near the centre of the model is set in motion by impulses so directed that all of them move together initially in the same direction and with the same velocity. It is evident that this would result in an elastic wave which would spread outwards from the centre towards the surface of the model and return again to the centre after travelling 15.4 kilometres in 24 hours, provided, of course, that in the course of this lengthy excursion, its energy has not dissipated itself completely. Then again, let us suppose that in another experiment, the same group of atoms is excited by two simultaneous sets of impulses so directed that the atoms belonging to the two interpenetrating Bravais lattices commence moving with equal velocities in opposite directions. In this case, it is easily seen that the result of the impulses would be to set up, not a travelling wave, but a local oscillation of the two lattices with respect to each other which would gradually spread outwards. Observations during a brief period of 60 seconds would suffice for a count of 2400 complete periods of the oscillation and hence also for a precise determination of its frequency. The presence of an external boundary many kilometers away from the centre of disturbance could obviously have no influence whatever on the phenomena taking place during those 60 seconds. In other words, the nature and frequency of the oscillation excited by the impulses would depend solely on the structure of the model and on no other considerations.

We may summarise the lessons taught by our model in the following two statements. (I) *The elastic vibrations in a crystal are a consequence of the translatory movements of its volume elements and therefore also of its lattice cells; they extend through the volume of the crystal, and their frequencies are low and form*

a diffuse continuous spectrum. (II) The characteristic vibrations in a crystal represent the internal oscillations of the units of its structure; they are highly localised and their frequencies are also high and have sharply defined values constituting a line-spectrum.

7. Born's lattice dynamics and its consequences

Whereas Debye restricted himself for the most part in his original paper to "monoatomic" solids, in other words to crystals having relatively simple structures, no such restriction is contemplated in the Born-Karman theory. Indeed, the claim made on behalf of the latter is that it specifically takes into account the lattice structure of the crystal and embraces in its scope the case of complex structures containing many atoms per unit cell. If there be p atoms in each cell, and N cells in the crystal, the total of $3Np$ degrees of atomic freedom of movement are identified with the same number of wave-patterns in the crystal. $3N$ wave-patterns represent the "acoustic" branches of the spectrum, and the remaining $(3p - 3)N$ wave-patterns the "optical" branches. Each wave-pattern is identified with one of the terms in a three-dimensional Fourier expansion, and the summation of all the terms with the totality of the possible vibrations in the crystal.

As has already been shown earlier in the paper, the identification of normal modes with wave-patterns is theoretically not a permissible procedure in the case of material media, and hence the entire structure of the Born lattice dynamics falls to the ground. It is unnecessary in these circumstances for us to consider the question dealt with in a paper by Ledermann¹¹ whether the so-called "cyclic postulate" is or is not an appropriate way of getting over the difficulty of the unknown boundary conditions at the external surface of a crystal. On the other hand, it might be useful to consider what the actual consequences of the Born lattice dynamics are in relation to the nature of the vibration spectra of crystals, so that we could proceed to compare them with the facts of experiment.

It is an immediate consequence of the Born-Karman theory that the vibration spectrum of a crystal presents the aspect of a diffuse continuum throughout the entire range of frequency. This is apparent from the numerous diagrams printed in Brillouin's book and from the calculations for various cases published by Born and his collaborators. The reason for it is also obvious. Since the wave-patterns from a Fourier sequence, their wavelengths are crowded together as we approach the limit where the sequence is assumed to be terminated and the wavelengths are therefore of the same order of magnitude as the lattice spacings of the crystal. A difference in wavelength necessarily means a change in frequency, and the variations thus arising become large for the "optical branches" of the spectrum near the lower limit of wavelength. Hence the frequency spectrum is spread out very widely in this region. But the spread is far from being negligible even in the

range of greater wavelengths. Though no actual calculations have been published for the case of crystals containing ions or molecules having their own characteristic frequencies of vibration, one may feel sure that if such calculations were made, the result would not exhibit any visible resemblance to the vibration spectra of such ions or molecules as we actually know them from experimental studies.

8. The scattering of light in crystals

For reasons which can well be understood, a crystal is intensely opaque to electromagnetic radiations over a wide range of frequency on either side of its own characteristic frequencies in the infra-red. In consequence, only rather vague and fragmentary indications were available regarding the nature of the vibration spectra of crystals, until the spectroscopic study of the scattering of light introduced a new and simple as well as powerful and accurate way of exploring this field of knowledge. From the analogies presented by the case of gases, liquids and amorphous solids where the same method is equally applicable, it is obvious that the frequency shifts observed in light scattering furnish us with a straight answer to the question of the nature of the vibration spectrum of a crystal, viz., that it consists of a set of sharply-defined monochromatic frequencies in the infra-red. The general acceptance of this simple view of the case has, however, been held up by the belief in theories which were put forward at a time when there was no experimental knowledge which could set theoretical thinking on the right path. To get over the patent contradiction between those theories and the experimental facts, it was suggested that while the real vibration-spectrum is continuous, the frequency shifts observed in light-scattering represent the result of the elimination of everything except the so-called limiting frequencies of vibration with large wavelengths by a selection principle based on the idea that the mechanical waves give a coherent reflection of the incident light waves, while the rest of the spectrum is hidden away from sight by a species of optical interference.

That the way proposed for escape from the difficulties is not a reasonable one becomes evident when it is recalled that large frequency shifts are also observed in the scattering of light by the molecules of gases and of liquids. They are very properly described in these cases as the result of an incoherent scattering in which the individual molecules of the substance exchange energy with the incident radiation. If this be a correct description of the process in the cases of fluid media, there is no reason why the obviously analogous effects observed with crystals should be regarded differently and ascribed to a coherent reflection of the light waves by mechanical waves. The mere change from a fluid to the solid state cannot be claimed as a justification, for it is found that organic glasses also give sharply-defined lines as frequency shifts in light-scattering. Such glasses are solids

in every sense of the term, and since they do not possess any periodicity of structure, it is not possible in their case to invoke any selection principle which could convert a diffuse continuum into a line spectrum.

Another observed fact which is absolutely fatal to the Born lattice dynamics is the appearance in numerous cases of sharply-defined lines as frequency shifts which do not agree with the fundamental frequencies of vibration, but are overtones or summations thereof. For frequency shifts of this kind to appear, it is essential that the amplitude of the atomic oscillations should be comparable with the interatomic distances, and this again would not be possible if the energy-quantum of the particular frequency is distributed as a wave extending over the whole volume of the crystal or even any limited region inside it. Overtones and summations could appear as frequency shifts with the observed intensities only if the oscillations are highly localised, in other words, are restricted to volumes which are comparable in their dimensions to the unit cells of the crystal structure. It is clearly not possible in these circumstances for the proposed selection principle to function which would pick up a single frequency from a continuous spectrum of frequencies.

Finally, we may refer to the specially interesting cases, of which diamond is the best example, in which strongly exposed spectrograms reveal frequency shifts appearing as sharply-defined lines which are not explicable as overtones or summations of the $(3p - 3)$ normal modes in which the phase is the same in adjacent lattice cells of the crystal lattice, but which compel the $21p$ additional modes in which the phase alternates also to be considered. Diamond, for instance, exhibits besides the line with a frequency shift of 2664 cm^{-1} which is the octave of the principal frequency of 1332 cm^{-1} , also several other lines as frequency shifts which are identifiable as overtones and summations of the eight fundamental frequencies of the diamond structure. In a recent paper in these *Proceedings*, P S Narayanan¹² has described and discussed the results of his studies on the case of diamond and shown that they are altogether incompatible with the consequences of the Born lattice dynamics. It is unnecessary to re-traverse the same ground here.

Summary

The enumeration of wave-patterns within an enclosure on a scale of wavelengths or frequencies presupposes that the waves are perfectly undamped and that the enclosure is perfectly reflecting. In any material medium, however, wave-propagation is necessarily damped and such damping may be so enormous as altogether to preclude wave-propagation. It follows that it is not permissible to identify the modes of atomic vibration in crystals with wave-patterns. Since the specific heat theories of Debye and of Born-Karman are based on such identification, they cannot be sustained.

For any mechanical model to represent the dynamic behaviour of a crystal, it is necessary that it should satisfy the requirements for dynamic similarity. When these requirements are satisfied, the behaviour of the model does not support the ideas underlying the Debye and Born–Karman theories, but on the other hand agrees with the results of the theory of the dynamics of crystal lattices put forward by the writer in 1943.

The phenomena of light-scattering observed in crystals are also discussed and it is shown that the experimental facts are incompatible with the ideas underlying the Born–Karman theory.

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The elasticity of crystals*

The materials used in engineering construction are mostly polycrystalline solids and their elastic behaviour is of the utmost practical importance. It follows that the subject of the elasticity of crystals is of more than merely academic interest. Of recent years the importance of its study has greatly been enhanced by several circumstances. The experimenter today can in many cases work with synthetically prepared crystals of large size and good quality. He has at his disposal several new techniques enabling him to determine their elastic behaviour and obtain precise results. These techniques are mostly based upon the production of waves or standing oscillations in the crystal with the aid of piezoelectric oscillators. These latter oscillators are themselves of importance in technical acoustics and communication engineering. The subject also stands in the closest relation to the structure of crystals as revealed by X-ray diffraction and spectroscopic studies. It is thus an integral part of the rapidly developing physics of the solid state.

2. The notions of stress and strain

The science of elasticity is based on the fundamental notions of stress and strain and—subject to a restriction on their magnitude—on the proportionality between them known as Hooke's law. The precise definition of stress and strain is thus a matter of fundamental importance. Such definitions have necessarily to be comprehensive. They have to cover cases where their magnitudes vary from point to point within the crystal and also cases in which the stresses and strains vary with time as in the theory of wave-propagation. It is essential, further, that they take account of the elastic anisotropy which all crystals exhibit, in other words, the fact that the effect of an impressed force depends on the direction in which it is applied.

An important remark which should be made here is that it is unnecessary to introduce atomistic considerations in defining stress or strain. This is obvious since the phenomena with which we are concerned are open to macroscopic

*1. "On the theory of the elasticity of crystals," by Sir C V Raman and Dr K S Viswanathan.

2. "Evaluation of the four elastic constants of some cubic crystals," by Sir C V Raman and D Krishnamurti. Memoir Nos. 73 and 76 of the Raman Research Institute, Bangalore, *Proc. Indian Acad. Sci.* **42**, 51 and 111 (1955).

observation. To take account of the variability of stress and strain with the location we define these quantities in relation to a particular point within the solid. The legitimacy of this procedure rests upon the fact that it is possible to imagine the volume of the substance to be divided into elements of such small dimensions that each element can be regarded as a mass particle and yet is large enough to justify its physical properties being assumed to be the same as those of the material in bulk. We are thereby enabled to specify the position of any volume element by its three co-ordinates in space and its state of equilibrium or of motion in terms of simple forces or tractions acting on the volume element.

3. The elastic constants

The foregoing remarks are preliminary to a specification of stress and strain which is logically consistent with the approach made to the subject. We define stress in terms of the tractive force assumed to act on an infinitesimal area drawn through a given point within the solid. Since this area can be set normal to each of the three co-ordinate axes in turn and for each such setting the acting force can be resolved into three components parallel to these axes respectively, we have nine components of stress. Likewise, strain is expressed in terms of the difference in displacements of two neighbouring points within the solid. Since the line joining these two points can be set parallel to each of the three co-ordinate axes in turn and the difference of their displacements in each case can itself be resolved along each of these axes in turn, we have nine components to deal with. The stress-strain relationships of proportionality would in the general case thus involve 9×9 or 81 elastic constants. The well known law of reciprocity which enables us to

Table 1

Crystal system	Point group (Schoenflies notation)	No. of elastic constants		
		General	Dynamic	Classical
Triclinic	All	45	36	21
Monoclinic	All	25	20	13
Orthorhombic	All	15	12	9
Tetragonal	C_4, S_4, C_{4h}	13	10	7
	$D_4, C_{4v}, D_{2d}, D_{4h}$	9	7	6
Trigonal	C_3, S_6	15	12	7
	D_3, C_{3v}, D_{3d}	10	8	6
Hexagonal	C_6, C_{3h}, C_{6h}	11	8	5
	$D_6, C_{6v}, D_{3h}, D_{6h}$	8	6	5
Cubic	T, T_h	5	4	3
	O, T_d, O_h	4	3	3

interchange the directions of force and displacement without change in the constant of proportionality between them results in the number 81 being reduced to $(9 + 36) = 45$ constants in all. Thus, it requires 45 elastic constants to describe the elastic behaviour of a triclinic crystal. For crystals of other classes, the number of independent constants is diminished by reason of their symmetry properties, the more so the higher the symmetry of the crystal. The number of independent elastic constants in each case can be readily worked out using the formulae based on group theory given by Bhagavantam. Table 1 exhibits the situation thus disclosed. The first column shows the symmetry class in the usual language of crystallography, while column 2 shows the subdivisions of those classes grouped together according to their elastic behaviour. The third column shows the number of independent elastic constants for these sub-classes.

4. Wave-propagation in crystals

Writing down the equations of motion of the volume of elements of the medium in terms of the space variations of the stress components acting upon them, one can investigate the propagation of waves through the material. It emerges that in any given direction within the solid, three types of waves can be propagated, their velocities being different in each case and also varying with the direction. The wave velocity for each of the three types and for any particular direction of propagation is expressible as a function of the direction and of certain linear combinations of the elastic constants. The number of these combinations is less than the number of general elastic constants in each case. The number can be calculated from formulae based on group theory and is shown in the fourth column of table 1.

5. Remarks on the classical theories

Cauchy, the celebrated French mathematician of the 19th century, in his memoir presented to the Academy of Sciences at Paris in the year 1822 proposed a reduction of the number of components of stress and strain from 9 to 6 in each case. His arguments will be found reproduced in numerous text-books and indeed they form the basis of the mathematical theory of elasticity as hitherto developed. A critical examination shows however that those arguments are not sustainable. In the case of the strain components, the reduction was sought to be justified by eliminating movements which were thought to be rigid body rotations. Actually the quantities eliminated are differential rotations of the same nature as those which appear in the deformation of solids by torsion or flexure and which are quite as much a part of the elastic deformations as extensions and contractions. Hence their elimination is not justified. The argument on which the reduction of

the number of stress components from 9 to 6 was based was that the angular momenta of the tractions acting on a volume element taken about each of the coordinate axes in turn and summed up should vanish. But since by definition the stresses are assumed to be in the nature of tractive forces acting on volume elements small enough to be regarded as single mass particles, no consideration of angular momenta is called for. Indeed, once we accept the definition of stress and strain, it becomes logically imperative to take account of all the nine components of each.

On the basis Cauchy's assumptions the stress-strain relations of proportionality are $6 \times 6 = 36$ in number and these by application of the reciprocity relationship reduce to $6 + 15 = 21$ in all for a triclinic crystal. Their number is smaller for the crystals of higher symmetry classes and is shown in column 5 of table 1 against each of them. The reduction in number of the stress and strain components from 9 to 6 is in effect equivalent to assuming that differential rotations within the solid play no part in the theory of elasticity and to imposing a corresponding restriction on the nature of the acting stresses. As already remarked, differential rotations play a fundamental role both in static deformations, especially in torsion, as also generally in wave-propagation. In other words, the classical theory is of restricted validity confined to certain types of static deformation and to particular cases of wave propagation. Since however it has been employed to interpret experimental data in other cases as well, it is useful to express the 21 constants in terms of the more general 45 constants, thereby enabling the latter to be evaluated from the existing data of experiments.

6. The data of experiment

As will be seen from table 1 the simplest cases of all are crystals belonging to the Td and the Oh classes of the cubic system. The general theory gives four elastic constants which may be designated as respectively d_{11} , d_{12} , d_{44} and d_{45} while in the classical theory we have only three constants which have been designated as C_{11} , C_{12} and C_{44} . The linear combinations of the elastic constants which determine the velocities of wave propagation are in the former theory d_{11} , d_{44} and $(d_{12} + d_{45})$ while in the classical theory they are C_{11} , C_{44} and $(C_{12} + C_{44})$. Likewise, the expressions for the bulk modulus in the new and the old theory are respectively $(d_{11} + 2d_{12})/3$ and $(C_{11} + 2C_{12})/3$. Since the number of elastic constants of these classes is four, while the number of linear combinations that can be determined by dynamic measurements is three, it follows that at least one additional determination by static methods is necessary to enable all the four constants to be evaluated. The most appropriate of such determinations appears to be the bulk-modulus of which very precise measurements have been made by Bridgman and his collaborators at Harvard. It is necessary of course to correct the isothermal static value of the constant to obtain the adiabatic bulk modulus.

Table 2. Elastic constants in 10^{11} dynes/cm².

Substance	C_{11}	C_{12}	C_{44}	d_{11}	d_{12}	d_{44}	d_{45}
NaCl	4.877	1.232	1.269	4.877	1.34	1.269	1.16
KCl	4.038	0.663	0.628	4.038	0.779	0.628	0.512
KBr	3.455	0.56	0.507	3.455	0.655	0.507	0.412
NaBr	3.87	0.97	0.97	3.87	1.22	0.97	0.72
LiF	11.9	5.38	5.34	11.9	4.5	5.34	6.22
MgO	28.76	8.74	15.14	28.76	11.27	15.14	12.61
AgCl	6.05	3.64	0.624	6.05	3.482	0.624	0.782
Diamond	95	39	43	95	35.9	43	46.1
Ge	12.88	4.825	6.705	12.88	4.04	6.705	7.49
Si	16.56	6.386	7.953	16.56	6.56	7.953	7.78
ZnS	10.79	7.22	4.12	10.79	6.17	4.12	5.17
CaF ₂	16.6	4.87	3.58	16.6	4.29	3.58	4.16
Al	10.56	6.39	2.853	10.56	6.29	2.853	2.953
Cu	16.92	12.25	7.55	16.92	12.81	7.55	6.99
Ni	25.26	15.51	12.3	25.26	16.01	12.3	11.8
Ag	12.4	9.34	4.61	12.4	8.89	4.61	5.06

Many other points have to be borne in mind: the bulk modulus reduced to zero pressures should be used; both the static and dynamic determinations have to be reduced to the same temperature of observation and finally the nature of the material used in the two cases has to be comparable.

In table 2 are shown, for 16 different crystals of the Td and Oh classes, the values of the four elastic constants calculated in the manner explained. The three constants of the older theory are also shown in the table. The latter are those which appeared to be the most reliable values obtained by ultrasonic techniques, while the former were obtained by combining them with the value for the adiabatic bulk-modulus. The values of C_{11} and d_{11} are in each case identical; likewise those of C_{44} and d_{44} . But C_{12} and d_{12} are different and such difference is a measure of the failure of the three-constant theory to represent the actual elastic behaviour of the crystal. The difference between d_{44} and d_{45} also expresses the same situation in another way.

Certain general features emerge from the table. For all the four alkali halides which are soluble in water, C_{12} is less than d_{12} and likewise d_{45} is less than d_{44} . The regularity of behaviour taken in conjunction with the reliability of the data in these cases makes it clear that these differences are real and justify us in concluding that the elastic behaviour of cubic crystals cannot be expressed in terms of three constants, but needs four. Diamond, germanium, zinc blende and fluorspar also exhibit a parallel behaviour which is the reverse of that shown by the four water-soluble alkali-halides. In their cases, C_{12} is decidedly greater than

d_{12} , while *per contra* d_{44} is less than d_{45} and these differences are numerically more striking than in the case of the alkali-halides. Magnesium oxide for which the data are reliable exhibits a noteworthy behaviour; the differences between C_{12} and d_{12} and likewise between d_{44} and d_{45} are in the same sense as in the alkali halides but proportionately much larger. Differences of the same order of magnitude but in the opposite sense is shown by lithium fluoride. In the case of the metals crystallizing in the face-centred cubic system, we also find differences between C_{12} and d_{12} and between d_{44} and d_{45} , but they are not always in the same sense. This is a feature which need not surprise us in view of the very great differences exhibited by these metals in other respects.

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The elastic behaviour of isotropic solids

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1. Introduction

It is a classic result in the phenomenological theory of elasticity that *two* independent constants suffice to describe the stress-strain relationships for an isotropic solid. If, for example, the bulk modulus and the shear modulus of the material are known, Young's modulus and Poisson's ratio may be calculated therefrom. In the present paper, the ideas regarding the nature of the strains and stresses in solids on which the derivation of this result is based are critically examined and it is shown that they are untenable. A re-formulation of the phenomenological theory of elasticity not open to the same objections is then presented and its consequences are developed. It emerges that *three* independent constants are needed to describe the stress-strain relationships of an isotropic body; in particular, it is shown that the bulk modulus of the material cannot be evaluated from the experimental data for the velocities of propagation of longitudinal and transverse waves respectively in the solid and its density.

2. Some general considerations

As is well known, the elastic constants of solids can be determined independently by static and dynamic methods. The latter are based on measurements of the velocity of propagation of waves of different types in the material. In all studies of this nature we are clearly concerned with *heterogeneous* strains, in other words with strains which are not of the same magnitude throughout the solid at any given instant; clearly, there could be no wave-propagation if the strains were the same everywhere. On the other hand, in the static methods of measuring elastic constants the strains may be homogeneous or heterogeneous according to the nature of the experiment. The change in volume of a solid under hydrostatic pressure is a case of the first kind, while the twisting of a rod by couples applied at its two ends is clearly a case of heterogeneous strain. The examples cited are sufficient to show that any theory of elastic behaviour has necessarily to concern

itself with *heterogeneous* strains; a theory which restricts itself to the consideration of homogeneous strains would be fundamentally incomplete.

The twisting of a rod by couples applied at its two ends also serves to illustrate certain fundamental aspects of the theory of elasticity. As just mentioned, it is an example of heterogeneous strain, and indicates that the movements of the parts of the solid in such strains may be angular movements or rotations, the magnitude of which varies through the volume of the solid. Thus, we are forced to recognize that the strains in a solid cannot, in general, be described solely as *elongations* but may also include *twists*. Further, in the case referred to, the external stresses applied to the body are *couples*. It follows that the internal stresses may also be of the same nature. In other words, the stresses in an elastic solid cannot be assumed to be exclusively in the nature of *tractive forces* but may also include *torques*.

The arguments in the classical theory of elasticity by which the familiar result quoted in the opening sentence of the paper are derived may be summed up briefly as follows: that it is sufficient to consider the case of homogeneous strains; that any homogeneous strain may be analysed into a "pure strain" and a rotation and that the latter should be ignored in formulating the stress-strain relationships; and finally that the tractive forces assumed to act on elements of area in the solid are so related that no torques tending to rotate the volume-elements of the solid are present. Everyone of these statements is at variance with the considerations set forth above. It follows that the argument with all its consequences is unacceptable.

3. Formulation of the theory

If now we denote by u_x, u_y, u_z the three components of the displacements of a point (x, y, z) of the material and by $u_x + u'_x, u_y + u'_y, u_z + u'_z$ the corresponding displacements of a neighbouring point situated at $(x + x', y + y', z + z')$, then it is a well known result that the strains in the neighbourhood of the point (x, y, z) can be represented by the scheme of equations

$$\begin{aligned} u_{x'} &= u_{xx}x' + u_{xy}y' + u_{xz}z' \\ u_{y'} &= u_{yx}x' + u_{yy}y' + u_{yz}z' \\ u_{z'} &= u_{zx}x' + u_{zy}y' + u_{zz}z' \end{aligned} \quad (1)$$

where u_{xy} stands, for brevity, for the differential coefficient $(\partial u_x / \partial y)$.

In view of what has been said in the previous section, all the nine components of strain figuring in the equations (1) are required for a complete specification of the deformations in which rotations are not ignored. Then the changes in the state of a volume element contemplated in (1) can be analysed into (i) changes of volume, (ii) changes in shape not involving rotations or alterations of volume, and (iii) rotations.

Likewise, the stresses in the interior of the solid require nine components for their full specification. Denoting by T_{xv} , T_{yv} and T_{zv} the components of the tractive forces parallel to the three axes of co-ordinates on any elementary area whose normal has a specified direction v , these tractions are related to the stresses acting on the three co-ordinate planes by means of the relations

$$\begin{aligned} T_{xv} &= T_{xx} \cos(x, v) + T_{xy} \cos(y, v) + T_{xz} \cos(z, v) \\ T_{yv} &= T_{yx} \cos(x, v) + T_{yy} \cos(y, v) + T_{yz} \cos(z, v) \\ T_{zv} &= T_{zx} \cos(x, v) + T_{zy} \cos(y, v) + T_{zz} \cos(z, v). \end{aligned} \quad (2)$$

As mentioned earlier, the three components of the angular momenta of any volume element will not vanish in dynamic experiments or for heterogeneous strains involving rotations and which accordingly involve torques. We therefore retain all the nine stress components in our formulation and do not make the usual reduction in their number from nine to six.

At this stage, we introduce a slight change in notation which enables us to pass on from symbols with double subscripts to symbols involving a single suffix only. We use for the stress components

$$T_{xx} T_{yy} T_{zz} T_{yz} T_{zy} T_{zx} T_{xz} T_{xy} T_{yx}$$

the symbols

$$T_1 T_2 T_3 T_4 T_5 T_6 T_7 T_8 T_9$$

respectively, and similarly write the strain variables

$$u_{xx} u_{yy} u_{zz} u_{yz} u_{zy} u_{zx} u_{xz} u_{xy} u_{yx}$$

as

$$u_1 u_2 u_3 u_4 u_5 u_6 u_7 u_8 u_9$$

respectively.

With this notation the stress-strain relations take a neat form. Since the stresses in the solid are dependent on the strain produced in the solid, the stress components can be expanded as a power series in the strain variables. If we measure the stresses from an initial state corresponding to the undeformed condition of the solid and consider infinitesimal strains only, so that squares and higher powers of the strain variables can be neglected in comparison with first order terms, the stresses at any point of the solid are linear functions of the strain components at that point. The stress-strain relations can then be expressed as

$$T_m = \sum_{n=1}^9 d_{mn} u_n \quad (m = 1, 2, \dots, 9) \quad (3)$$

and these involve 81 constants. Here the constant d_{mn} relates the stress T_m to the

strain u_n and is the ratio of the two for a deformation in which all strain components other than u_n vanish.

The 81 constants figuring in (3) are not all independent, but reduce in the first instance to forty-five for all solids in view of the relations

$$d_{mn} = d_{nm} (m, n = 1, 2, \dots, 9). \quad (4)$$

These relations follow from the well known theorem of reciprocity relating forces and the corresponding displacements in dynamical systems⁴. The reciprocity relations further enable us to write down the expression for the deformation energy per unit volume in the neighbourhood of any point and this is given by

$$U = \frac{1}{2} \sum_{m=1}^9 T_m u_m$$

or

$$2U = \sum_m \sum_n d_{mn} u_m u_n. \quad (5)$$

4. The three elastic constants of isotropic solids

The isotropic nature of a body results in a great reduction of the number of independent constants occurring in the stress-strain relationships. Most of these constants in fact are zero and the others become equal to each other in sets for isotropic materials. Some of these relations can be deduced easily from simple symmetry considerations, without going into the full details of the analytic apparatus needed to derive them. For example, the cubic symmetry possessed by the material endows it with the same property for all the three directions of the axes of co-ordinates and therefore the stress-relationships should remain invariant under any permutation of the symbols x, y, z in both the strain variables (u_{xy}) as well as in the stress components T_{xy} . We thus get

$$\begin{aligned} d_{11} &= d_{22} = d_{33}; \\ d_{12} &= d_{23} = d_{31}; \\ d_{45} &= d_{67} = d_{89}; \\ d_{44} &= d_{55} = d_{66} = d_{77} = d_{88} = d_{99}. \end{aligned} \quad (6)$$

Again, the operations of reflection about any plane in space do not produce observable changes in the properties of isotropic bodies. In the simple case of a reflection about the xy plane, the z co-ordinate of any point changes its sign while its x and y co-ordinates are unaffected. Hence all the strain components like $u_{yz}(u_4), u_{zy}(u_5), u_{zx}(u_6), u_{xz}(u_7)$ in which z occurs *once* only as a suffix change their sign whereas the other strain variables are unaltered. If therefore we substitute these new values of the strain variables in the energy expression and equate it to

the original one, we get

$$\begin{aligned} d_{14} = d_{15} = d_{16} = d_{17} = d_{24} = d_{25} = d_{26} = d_{27} = d_{34} = d_{35} \\ = d_{36} = d_{37} = d_{48} = d_{49} = d_{58} = d_{59} = d_{68} = d_{69} = d_{78} = d_{79} = 0. \end{aligned} \quad (7)$$

Similarly by considering reflections about the planes $x = 0$, and $y = 0$, we could show that

$$d_{18} = d_{19} = d_{28} = d_{29} = d_{38} = d_{39} = d_{46} = d_{47} = d_{56} = d_{57} = 0. \quad (8)$$

Simple symmetry considerations thus reduce the number of non-zero and independent constants to four. Even these constants i.e., d_{11} , d_{12} , d_{44} and d_{45} however are not independent but are connected to each other by means of a linear relation. To obtain this, we use the special symmetry property possessed by isotropic solids alone, namely invariance in behaviour under all rotations in space. Considering a rotation about the z -axis through an angle θ , this operation changes the strain variables into a new set of quantities $u'_1, u'_2 \dots u'_9$ related to the original ones in accordance with the following scheme:

$$\begin{aligned} u'_1 &= u_1 \cos^2 \theta + (u_8 + u_9) \sin \theta \cos \theta + u_2 \sin^2 \theta; \\ u'_2 &= u_1 \sin^2 \theta - (u_8 + u_9) \sin \theta \cos \theta + u_2 \cos^2 \theta; \\ u'_3 &= u_3; \\ u'_4 &= u_4 \cos \theta - u_7 \sin \theta; \\ u'_5 &= u_5 \cos \theta - u_6 \sin \theta; \\ u'_6 &= u_5 \sin \theta + u_6 \cos \theta; \\ u'_7 &= u_4 \sin \theta + u_7 \cos \theta; \\ u'_8 &= (u_2 - u_1) \sin \theta \cos \theta + (u_8 \cos^2 \theta - u_9 \sin^2 \theta); \\ u'_9 &= (u_2 - u_1) \sin \theta \cos \theta + (u_9 \cos^2 \theta - u_8 \sin^2 \theta). \end{aligned} \quad (9)$$

Hence under the operation of a rotation about the z -axis by an amount θ , the energy expression (5) changes into

$$\begin{aligned} 2U &= d_{11}u_3^2 + d_{11}\{u_1 \cos^2 \theta + (u_8 + u_9) \sin \theta \cos \theta + u_2 \sin^2 \theta\}^2 \\ &+ d_{11}\{u_1 \sin^2 \theta - (u_8 + u_9) \sin \theta \cos \theta + u_2 \cos^2 \theta\}^2 \\ &+ 2d_{12}(u_1 + u_2)u_3 \\ &+ 2d_{12}\{u_1 \cos^2 \theta + (u_8 + u_9) \sin \theta \cos \theta + u_2 \sin^2 \theta\} \\ &\quad \times \{u_1 \sin^2 \theta - (u_8 + u_9) \sin \theta \cos \theta + u_2 \cos^2 \theta\} \\ &+ d_{44}\{(u_2 - u_1) \sin \theta \cos \theta + u_8 \cos^2 \theta - u_9 \sin^2 \theta\}^2 \\ &+ d_{44}\{(u_2 - u_1) \sin \theta \cos \theta + u_9 \cos^2 \theta - u_8 \sin^2 \theta\}^2 \\ &+ d_{44}(u_4^2 + u_5^2 + u_6^2 + u_7^2) + 2d_{45}(u_4u_5 + u_6u_7) \\ &+ 2d_{45}\{(u_2 - u_1) \sin \theta \cos \theta + u_8 \cos^2 \theta - u_9 \sin^2 \theta\} \\ &\quad \times \{(u_2 - u_1) \sin \theta \cos \theta + u_9 \cos^2 \theta - u_8 \sin^2 \theta\}. \end{aligned} \quad (10)$$

Comparing this with the expression

$$\begin{aligned}
 2U = & d_{11}(u_1^2 + u_2^2 + u_3^2) + 2d_{12}(u_2u_3 + u_3u_1 + u_1u_2) \\
 & + d_{44}(u_4^2 + u_5^2 + u_6^2 + u_7^2 + u_8^2 + u_9^2) \\
 & + 2d_{45}(u_4u_5 + u_6u_7 + u_8u_9)
 \end{aligned} \tag{11}$$

we get

$$d_{11} = d_{12} + d_{44} + d_{45} \tag{12}$$

Rotations about the x - and y -axes through any angle should also necessarily lead to the same equation (12). A general rotation about any axis can be effected by a superposition of rotations through different angles about the x , y and z axes. We have thus exhausted all the symmetry operations permissible for isotropic solids. It follows therefore that *the elastic behaviour of isotropic solids requires three independent constants for its description, which may be denoted by d_{11} , d_{12} and d_{44} .*

5. Relations between the various constants

With the aid of the relations (6), (7), (8) and (12), the stress-strain relationships described by (12) can be rewritten. The expressions for the three stretches T_1 , T_2 and T_3 become

$$\begin{aligned}
 T_1 &= d_{11}u_1 + d_{12}(u_2 + u_3) \\
 T_2 &= d_{11}u_2 + d_{12}(u_3 + u_1) \\
 T_3 &= d_{11}u_3 + d_{12}(u_1 + u_2)
 \end{aligned} \tag{13}$$

whereas the shearing stresses are given by

$$\begin{aligned}
 T_4 &= d_{44}u_4 + (d_{11} - d_{12} - d_{44})u_5 \\
 T_5 &= d_{44}u_5 + (d_{11} - d_{12} - d_{44})u_4
 \end{aligned} \tag{14}$$

and four similar equations.

We shall now evaluate some of the important elastic constants, viz., the compressibility or bulk modulus, Young's modulus and Poisson's ratio in terms of these new constants. Consider first the case of a uniform hydrostatic pressure acting at all points on the surface of the body. The state of stress produced by such a compression of the solid is described by $T_1 = T_2 = T_3 = -p$; $T_4 = T_5 = \dots = T_9 = 0$. Hence adding all the three equations in (13), we get

$$p = \frac{1}{3}(d_{11} + 2d_{12})\Delta \tag{15}$$

where Δ denotes the cubical compression $-(u_1 + u_2 + u_3)$. The bulk modulus therefore is given by

$$k = \frac{1}{3}(d_{11} + 2d_{12}). \tag{16}$$

Similarly by considering the case of an isotropic body in the form of a

cylindrical rod subjected to a tension T which is uniform over its plane ends, we could show that the Young's modulus E and Poisson's ratio σ are related to d_{11} and d_{12} in accordance with the equations

$$E = \frac{(d_{11} + 2d_{12})(d_{11} - d_{12})}{(d_{11} + d_{12})} \quad (17)$$

$$\sigma = \frac{d_{12}}{(d_{11} + d_{12})}. \quad (18)$$

These expressions are in the same form as the corresponding ones for k , E and σ of the classical theory expressed in terms of the well known constants c_{11} and c_{12} . The relations among the Young's modulus, bulk modulus, and Poisson's ratio are therefore the same both in the two-constant as well as in the three-constant theories. We emphasize the fact that all the three equations (16), (17) and (18) contain the constants d_{11} and d_{12} only, and none of them involves d_{44} explicitly. This is because all these moduli are determinable from static homogeneous strains alone, whereas d_{44} , being a constant involving rotations of the volume elements requires experiments involving twists for its evaluation.

It may be pointed out here that the relation (12) may be derived directly from very simple considerations. A cube which is subject to normal tractions on a pair of opposing faces and normal pressures of equal magnitude on an adjacent pair of faces would suffer no change of volume, but would expand and contract respectively in the direction of the two normals to the faces by an amount of which $(d_{11} - d_{12})$ is a measure. Likewise, if a pair of opposing faces of a cube are subject to tangential tractions forming a couple and an adjacent pair also subject to tangential tractions which form a balancing couple, the cube would suffer no change of volume but would undergo a change of shape without rotation of which $(d_{44} + d_{45})$ is readily seen to be a measure. The two systems of stresses and the resulting strains can readily be shown to be equivalent and it follows that $(d_{11} - d_{12}) = (d_{44} + d_{45})$.

6. Velocity of propagation of waves in the solid

In the absence of body forces, the general equations of motion of an elastic body are given by

$$\begin{aligned} \rho \frac{\partial^2 u_x}{\partial t^2} &= \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z}; \\ \rho \frac{\partial^2 u_y}{\partial t^2} &= \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z} \\ \rho \frac{\partial^2 u_z}{\partial t^2} &= \frac{\partial T_{zx}}{\partial x} + \frac{\partial T_{zy}}{\partial y} + \frac{\partial T_{zz}}{\partial z} \end{aligned} \quad (19)$$

where ρ is the density of the material. For an isotropic solid, the stress-strain relations are given by equations (13) and (14). Adopting once again the primitive notation of writing differential coefficients $\partial u_x/\partial x, \dots, \partial u_y/\partial z, \dots$ for the strain components u_1, \dots, u_4, \dots etc., we get on substituting (13) and (14) in (19) that

$$\begin{aligned} \rho \frac{\partial^2 u_x}{\partial t^2} = & (d_{11} - d_{12}) \nabla^2 u_x + d_{12} \frac{\partial \Delta}{\partial x} \\ & + (d_{11} - d_{12} - d_{44}) \left\{ \frac{\partial}{\partial z} \left(\frac{\partial u_z}{\partial x} - \frac{\partial u_x}{\partial z} \right) - \frac{\partial}{\partial y} \left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right) \right\} \end{aligned} \quad (20)$$

and two similar equations for the displacements in the y and z directions. In the above, Δ denotes the dilatation

$$\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right)$$

or simply divergence \mathbf{u} where \mathbf{u} is the vector whose components parallel to the axes are u_x, u_y and u_z respectively. The three equations in (20) can be combined together and written as a single equation in the form

$$\begin{aligned} \rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = & (d_{11} - d_{12}) \nabla^2 \mathbf{u} + d_{12} \text{grad div } \mathbf{u} \\ & + (d_{11} - d_{12} - d_{44}) \text{curl curl } \mathbf{u} \end{aligned} \quad (21)$$

Since $\text{curl curl } \mathbf{u} = \text{grad div } \mathbf{u} - \nabla^2 \mathbf{u}$, (21) alternatively becomes

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = d_{44} \nabla^2 \mathbf{u} + (d_{11} - d_{44}) \text{grad div } \mathbf{u}. \quad (22)$$

We shall now take the *divergence* of both sides of (22). This gives us

$$\rho \frac{\partial^2 \Delta}{\partial t^2} = d_{11} \nabla^2 \Delta. \quad (23)$$

The above is in fact the equation of wave propagation in the medium. *Compressional waves are therefore propagated in the solid with the velocity $\sqrt{d_{11}/\rho}$.*

Performing next the operation of *curl* on both sides of (22), and writing ω for $\text{curl } \mathbf{u}$, one gets

$$\rho \frac{\partial^2 \omega}{\partial t^2} = d_{44} \nabla^2 \omega. \quad (24)$$

equation (24) therefore shows that *equivoluminal or distortional waves are propagated in the medium with the velocity $\sqrt{d_{44}/\rho}$.*

It will be noticed that the velocities of propagation of both the longitudinal and transverse waves determine the constants d_{11} and d_{44} only, and do not involve the

constant d_{12} at all. On the other hand, d_{44} does not make its appearance in the moduli determinable by static homogeneous strains.

7. Summary

The notions regarding stresses and strains adopted in the classical theory of elasticity are critically examined. The neglect of rotations in the analysis of strain and of torques in the analysis of stress characteristic of that theory is shown to be unjustifiable. A reformulation of the stress-strain relationships taking account of these factors leads to the result that an isotropic solid has *three* independent elastic constants and not *two* as hitherto supposed. Two of these three constants determine the velocities of propagation respectively of longitudinal and transverse waves in the solid. The latter of them does not make its appearance in any observations involving only homogeneous strains nor does it appear in the formulae for the bulk modulus, Young's modulus and Poisson's ratio obtained in the present paper.

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On the theory of the elasticity of crystals

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1. Introduction

The branch of mathematical physics known as the theory of the elasticity of solids is based on certain notions regarding elastic stresses and strains which have been accepted doctrine for many years. It is therefore rather surprising to find that those notions are not sustainable and that the theory based on them has to be laid aside in favour of a stricter formulation. The need for such revision was broadly indicated in a recent publication in these *Proceedings* by the present authors (1955); but in view of the importance of the matter, the present paper is prefaced by a clearer and more precise exposition of the necessity for a revision of the classical theory.

Our recent paper dealt with the case of isotropic solids in a formal manner, considering them as homogeneous substances exhibiting the highest possible symmetry in their elastic properties. Usually, however, the so-called isotropic solids are merely polycrystalline aggregates, and a discussion of their elastic behaviour should therefore properly be based on a consideration of the nature and properties of such aggregates. This is a task which we hope to be able to address ourselves in the not-too-distant future. In the present paper we shall consider the case of truly homogeneous but anisotropic solids, in other words, crystals. The subject will be dealt with from the phenomenological standpoint since this proves to be entirely adequate. We may remark, however, that the conclusions reached are in complete accord with the results of the atomistic approach to the theory of elasticity as developed both from the static and dynamic standpoints in a paper by one of us (Viswanathan, 1954) and illustrated by a detailed discussion of a particular case of great interest, viz., diamond.

2. The physical characters of elastic stress and strains

A solid body may be defined as a material in which the volume elements retain their relative positions and orientations alike when the solid is at rest and when it is in a state of movement, translatory or rotatory, as the case may be. Elastic

stresses and strains arise when the situation thus described is departed from to ever so small an extent. Hence, it is evident that the theory of elasticity is concerned with changes in the relative orientations of the volume elements of the solid, in other words, with linear displacements and/or angular movements of the volume elements with respect to their neighbours. This is illustrated by the familiar examples of a straight bar which is stretched or bent or twisted by the application of appropriate external stresses. From the general considerations indicated above as well as from the particular examples mentioned, it is clear that only in very special cases would elastic strains be such that a straight line drawn through the solid in any direction in the unstrained condition remains straight in the strained state, suffering only elongations or contractions. In the general case, and inevitably so when the strains involve differential rotations, a straight line in the unstrained condition would be curved in the strained state, and such curvature cannot possibly be ignored in the theory. Hence, it is clear that we have, in general, to consider strains and stresses which are heterogeneous, in other words, strains and stresses whose specifications vary from point to point within the solid. These variations necessarily enter into the equations of equilibrium in the static state and into the equations of motion in dynamic behaviour.

3. Analytical specification of stresses and strains

The mathematical theory of elasticity proceeds on the basis that the strains and stresses in the interior of the solid can be expressed in terms of the movements of the smallest possible elements of volume into which it can be imagined to be subdivided and of the forces acting on them. If the volume elements be small enough, their movements can be described completely in terms of the three positional co-ordinates of each element and their variations. Likewise, when the elements of volume are small enough, the interactions between each element and its neighbours can be expressed in terms of tractive forces alone, it being then clearly unnecessary to introduce anything in the nature of couples or torques. On the basis of these ideas, the state of strain in the solid at any given point can be expressed by resolving the displacement of the elementary volume originally located at such point along three mutually perpendicular directions and differentiating these three components of displacement again along each of the three axes in turn. We thus obtain the nine components of the strain tensor. Likewise, for specifying the state of stress to which the volume element is subject, we consider the tractive forces acting on an infinitesimal area drawn respectively normal to the three co-ordinate planes in turn at the position of the element and then again resolve these tractive forces along each of the three co-ordinate axes. We thus obtain the nine components of the stress tensor.

It is evident that this method of representation of the stresses and strains

uniquely defines the state of the solid at any point and also enables us to determine whether the element of volume would or would not remain in equilibrium. If the components of stress do not vary along any of the three axes, the element would necessarily remain at rest. If, on the other hand, the stress components vary, their differential coefficients along the normals to the planes on which they act gives us a measure of the forces on the volume element in their respective directions. Adding up the three forces along each axis thus evaluated and putting their sums separately equal to zero, we obtain the conditions of equilibrium.

The well known and familiar treatments given in the standard treatises proceed on the basis that the components of the strain and stress tensors are both reducible in number from nine to six. The arguments on which the reduction in number from nine to six of the components of strain is based may be summarised by the statement that the elastic strains can be separated into what are called "pure strains" and "rotations," and that the latter can be ignored. That this argument is unsustainable will be evident at once from the remarks made in the foregoing section regarding the physical nature of elastic strains. We have, in general, to take account of both differential displacements and differential rotations and it is therefore not permissible to eliminate the rotational parts of the strain, these being physically quite as real as the irrotational parts.

The arguments justifying the reduction in the number of the independent components of stress from nine to six are based upon the idea that equilibrium would be possible only if the angular momenta of the tractions taken about each of the three co-ordinate axes in turn cancel each other out. That this idea is misconceived will be evident from the remarks already made earlier regarding the conditions necessary for equilibrium. In the case of homogeneous strains, the tractive forces acting on each volume element necessarily balance each other. In the case of heterogeneous strains, the conditions of equilibrium can be expressed in terms of the differential coefficients of the stress components along the normals to the planes on which they act, as already explained. In either case, if the equilibrium conditions for each volume element of the solid are satisfied, then the solid as a whole necessarily remains in equilibrium; vice versa, if the external stresses acting on the solid are such that it remains as a whole in equilibrium, the elastic stresses would everywhere necessarily be such as to ensure equilibrium of the individual volume elements. It follows that no general relations connecting the magnitude of the tensor components and enabling their number to be reduced from nine to six can be derived from considerations based on the conditions for equilibrium.

We may summarise our conclusions by stating that neither the reduction of the strain components nor the reduction of the stress components in number from nine to six has any theoretical justification; a correct and complete theory of elasticity has necessarily to take all the nine components of the stress and strain tensors into consideration.

4. The stress-strain relationships

Writing the nine components of the strain tensor as

$$\begin{array}{ccccccccc} u_{xx} & u_{yy} & u_{zz} & u_{yz} & u_{zy} & u_{zx} & u_{xz} & u_{xy} & u_{yx} \\ u_1 & u_2 & u_3 & u_4 & u_5 & u_6 & u_7 & u_8 & u_9 \end{array}$$

and likewise the nine components of the stress tensor as

$$\begin{array}{ccccccccc} T_{xx} & T_{yy} & T_{zz} & T_{yz} & T_{zy} & T_{zx} & T_{xz} & T_{xy} & T_{yx} \\ T_1 & T_2 & T_3 & T_4 & T_5 & T_6 & T_7 & T_8 & T_9 \end{array}$$

the stress-strain relations can be expressed in the general form

$$T_m = \sum_{n=1}^9 d_{mn} u_n \quad (m = 1, 2, \dots, 9) \quad (1)$$

and involve 81 constants. Here the constant d_{mn} relates the stress T_m to the strain u_n and is the ratio of the two for a deformation in which all components other than u_n vanish.

The 81 constants figuring in (1) are not all independent, but reduce in the first instance to forty-five for all solids in view of the relations

$$d_{mn} = d_{nm} \quad (m, n = 1, 2, \dots, 9). \quad (2)$$

The above relations follow from the well known theorem of reciprocity relating forces and the corresponding displacements of dynamical systems. The reciprocity relations further enable us to write down the expression for the deformation energy per unit volume in the neighbourhood of any point and this is given by

$$U = \frac{1}{2} \sum_{m=1}^9 T_m u_m$$

or

$$2U = \sum_m \sum_n d_{mn} u_m u_n. \quad (3)$$

Thus in the general case of a completely anisotropic solid, we have forty-five elastic constants instead of the 21 contemplated by the classical theory.

The number of independent elastic constants which is forty-five for a completely anisotropic solid diminishes in the case of solids possessing the various elements of symmetry characteristic of the different crystal classes, coming down to four for crystals of the classes T_d , O and O_h . The number of surviving constants in each symmetry class can be computed in an elegant fashion by adopting the group-theoretical method developed by Bhagavantam (1949). One is concerned in the present case with a linear relationship between nine stress components and nine strain components, the constants of proportionality being the elastic constants (matrix d_{mn}). Further, the elements of the "elastic constants 9

by 9 matrix" satisfy the relation $d_{mn} = d_{nm}$. With these restrictions, the transformation matrix for the elastic constants can be written out and the corresponding character can be deduced. This comes out as

$$\chi'_j(\mathbf{R}) = 16c^4 \pm 16c^3 + 8c^2 \pm 4c + 1 \quad (4)$$

where $c = \cos \phi$, \mathbf{R} is a symmetry operation and ϕ , the rotation. The *plus* sign is used for proper rotations, and *minus* for an improper one. The corresponding character for the 21-constant theory is

$$\chi'_j(\mathbf{R}) = 16c^4 \pm 8c^3 - 4c^2 + 1 \quad (5)$$

Table 1 gives the number of independent constants according to the two formulae for each symmetry class, while the constants that survive and those that vanish

Table 1

Crystal system	Point group	No. of elastic constants	
		I	II
Triclinic	All	21	45
Monoclinic	All	13	25
Orthorhombic	All	9	15
Tetragonal	$C_4(4)$ $S_4(\bar{4})$ $C_{4h}(4/m)$ }	7	13
	$D_4(422)$ $C_{4v}(4mm)$ $S_{4v} = D_{2d}(42m)$ $D_{4h}(4/m2/m2/m)$ }	6	9
Trigonal	$C_3(3)$ $S_6(\bar{3})$ }	7	15
	$D_3(32)$ $C_{3v}(3m)$ $D_{3d}(\bar{3}2/m)$ }	6	10
Hexagonal	$C_6(6)$ $C_{3h}(\bar{6})$ $C_{6h}(6/m)$ }	5	11
	$D_6(622)$ $C_{6v}(6mm)$ $D_{3h}(\bar{6}m2)$ $D_{6h}(6/m2/m2/m)$ }	5	8
Cubic	$T(23)$ $T_h(2/m\bar{3})$ }	3	5
	$O(432)$ $T_d(\bar{4}3m)$ $O_h(4/m\bar{3}2/m)$ }	3	4

are exhibited in detail for the various cases in tables 2 to 12. A comparison of these tables amongst themselves will enable the reader to realise how the existence of common symmetry elements results in the appearance of common features in the tables of elastic constants. For example, all the twenty constants that vanish for

Table 2

<i>Triclinic (C_1, C_i)</i>								
d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	d_{19}
	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}	d_{27}	d_{28}	d_{29}
		d_{33}	d_{34}	d_{35}	d_{36}	d_{37}	d_{38}	d_{39}
			d_{44}	d_{45}	d_{46}	d_{47}	d_{48}	d_{49}
				d_{55}	d_{56}	d_{57}	d_{58}	d_{59}
					d_{66}	d_{67}	d_{68}	d_{69}
						d_{77}	d_{78}	d_{79}
							d_{88}	d_{89}
								d_{99}

45 constants

Table 3

<i>Monoclinic (C_s, C_2, C_{2h})—diad axis $\parallel z$, plane of reflection \perp to z</i>								
d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	d_{19}
	d_{22}	d_{23}	0	0	0	0	d_{28}	d_{29}
		d_{33}	0	0	0	0	d_{38}	d_{39}
			d_{44}	d_{45}	d_{46}	d_{47}	0	0
				d_{55}	d_{56}	d_{57}	0	0
					d_{66}	d_{67}	0	0
						d_{77}	0	0
							d_{88}	d_{89}
								d_{99}

25 constants

Table 4

<i>Orthorhombic (C_{2v}, D_2, D_{2h})</i>								
d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{22}	d_{23}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{66}	d_{67}	0	0
						d_{77}	0	0
							d_{88}	d_{89}
								d_{99}

15 constants

Table 5

<i>Tetragonal</i> (C_4, S_4, C_{4h})—tetrad axis $\parallel z$								
d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	d_{19}
	d_{11}	d_{13}	0	0	0	0	$-d_{19}$	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	0	0
				d_{55}	0	$-d_{46}$	0	0
					d_{55}	d_{45}	0	0
						d_{44}	0	0
							d_{88}	d_{89}
								d_{88}

13 constants

Table 6

<i>Tetragonal</i> ($C_{4v}, S_{4v}, D_4, D_{4h}$)—tetrad axis $\parallel z$								
d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{11}	d_{13}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{55}	d_{45}	0	0
						d_{44}	0	0
							d_{88}	d_{89}
								d_{88}

9 constants

Table 7

<i>Trigonal</i> (C_3, S_6)—triad axis $\parallel z$								
d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}	d_{17}	d_{18}	$-d_{18}$
	d_{11}	d_{13}	$-d_{14}$	$-d_{15}$	$-d_{16}$	$-d_{17}$	d_{18}	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	d_{17}	$-d_{17}$
				d_{55}	0	$-d_{46}$	$-d_{16}$	$-d_{16}$
					d_{44}	d_{45}	d_{15}	d_{15}
						d_{55}	d_{14}	d_{14}
							d_{88}	d_{89}
								d_{88}

$$d_{88} = d_{11} - d_{12} - d_{89}$$

15 constants

monoclinic crystals also disappear in the orthorhombic, tetragonal and cubic systems. Likewise, all the thirty constants that vanish for orthorhombic crystals vanish also for those tetragonal crystals which possess three mutually perpendicular diad axes and for all cubic crystals. A noteworthy feature is that the

Table 8

<i>Trigonal (D₃, D_{3d}, C_{3v})—triad axis z</i>								
d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	0	0	0	0
	d_{11}	d_{13}	$-d_{14}$	$-d_{15}$	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	d_{15}	d_{15}
$d_{88} = d_{11} - d_{12} - d_{89}$						d_{55}	d_{14}	d_{14}
10 constants							d_{88}	d_{89}
							d_{88}	d_{88}

Table 9

<i>Hexagonal (C_{3h}, C₆, C_{6h})—hexad axis z</i>								
d_{11}	d_{12}	d_{13}	0	0	0	0	d_{18}	$-d_{18}$
	d_{11}	d_{13}	0	0	0	0	d_{18}	$-d_{18}$
		d_{33}	0	0	0	0	d_{38}	$-d_{38}$
			d_{44}	d_{45}	d_{46}	0	0	0
				d_{55}	0	$-d_{46}$	0	0
					d_{44}	d_{45}	0	0
$d_{88} = d_{11} - d_{12} - d_{89}$						d_{55}	0	0
11 constants							d_{88}	d_{89}
							d_{88}	d_{88}

Table 10

<i>Hexagonal (D_{3h}, C_{6v}, D₆, D_{6h})—hexad axis z</i>								
d_{11}	d_{12}	d_{13}	0	0	0	0	0	0
	d_{11}	d_{13}	0	0	0	0	0	0
		d_{33}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	0	0
$d_{88} = d_{11} - d_{12} - d_{89}$						d_{55}	0	0
8 constants							d_{88}	d_{89}
							d_{88}	d_{88}

Table 11

Cubic (T, T _h)								
d_{11}	d_{12}	d_{12}	0	0	0	0	0	0
	d_{11}	d_{12}	0	0	0	0	0	0
		d_{11}	0	0	0	0	0	0
			d_{44}	d_{45}	0	0	0	0
				d_{55}	0	0	0	0
					d_{44}	d_{45}	0	0
						d_{55}	0	0
							d_{44}	d_{45}
								d_{55}

5 constants

Table 12

Cubic (T _d , O, O _h)								
d_{11}	d_{12}	d_{12}	0	0	0	0	0	0
	d_{11}	d_{12}	0	0	0	0	0	0
		d_{11}	0	0	0	0	0	0
			d_{14}	d_{45}	0	0	0	0
				d_{44}	0	0	0	0
					d_{44}	d_{45}	0	0
						d_{44}	0	0
							d_{44}	d_{45}
								d_{44}

4 constants

cubic crystals which exhibit a four-fold axis of symmetry have only four different elastic constants, whereas those cubic crystals that do not exhibit this feature have five constants different from each other.

5. Wave-propagation in crystals

The general equations of motion of an elastic solid are given by

$$\begin{aligned}
 \rho \frac{\partial^2 u_x}{\partial t^2} &= \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} \\
 \rho \frac{\partial^2 u_y}{\partial t^2} &= \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z} \\
 \rho \frac{\partial^2 u_z}{\partial t^2} &= \frac{\partial T_{zx}}{\partial x} + \frac{\partial T_{zy}}{\partial y} + \frac{\partial T_{zz}}{\partial z}
 \end{aligned}
 \tag{6}$$

where ρ is the density of the medium and T_{xx}, \dots are the stress components. If the solid is in equilibrium, the quantities on the left-hand side of these equations, representing the acceleration of an unit volume element, will vanish and we get the conditions of equilibrium of the solid.

To evaluate the velocity of propagation of waves in the solid in any given direction, we first seek solutions of the above equations which are in the form of plane waves of the type

$$\mathbf{u} = \mathbf{A} \exp i \frac{2\pi}{\lambda} (vt - \mathbf{e} \cdot \mathbf{r}). \quad (7)$$

Denoting the components of \mathbf{A} in the directions of the co-ordinate axes by $\mathbf{A}^x, \mathbf{A}^y, \mathbf{A}^z$ and using once again the four-suffixed symbols for the elastic constants, we now get on substitution of (7) in (6) that

$$\rho v^2 \mathbf{A}^x = \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},y\bar{y}} \mathbf{e}_{x\bar{x}} \mathbf{e}_{y\bar{y}} \mathbf{A}^y \quad (8)$$

and two similar equations for the y and z components.

For a wave progressing in the direction (lmn) equation (8) can alternatively be written as

$$\begin{aligned} (\lambda_{xx} - \rho v^2) \mathbf{A}^x + \lambda_{xy} \mathbf{A}^y + \lambda_{xz} \mathbf{A}^z &= 0 \\ \lambda_{xy} \mathbf{A}^x + (\lambda_{yy} - \rho v^2) \mathbf{A}^y + \lambda_{yz} \mathbf{A}^z &= 0 \\ \lambda_{xz} \mathbf{A}^x + \lambda_{yz} \mathbf{A}^y + (\lambda_{zz} - \rho v^2) \mathbf{A}^z &= 0 \end{aligned} \quad (9)$$

where $\lambda_{xx}, \lambda_{xy}, \dots$ are given by the scheme

$$\begin{pmatrix} \lambda_{xx} \\ \lambda_{yy} \\ \lambda_{zz} \\ \lambda_{yz} \\ \lambda_{zx} \\ \lambda_{xy} \end{pmatrix} = \begin{pmatrix} d_{11} & d_{88} & d_{77} & 2d_{78} & 2d_{17} & 2d_{18} \\ d_{99} & d_{22} & d_{44} & 2d_{24} & 2d_{49} & 2d_{29} \\ d_{66} & d_{55} & d_{33} & 2d_{35} & 2d_{36} & 2d_{56} \\ d_{69} & d_{25} & d_{34} & (d_{23} + d_{45}) & (d_{39} + d_{46}) & (d_{59} + d_{26}) \\ d_{16} & d_{58} & d_{37} & (d_{57} + d_{38}) & (d_{67} + d_{13}) & (d_{15} + d_{68}) \\ d_{19} & d_{28} & d_{47} & (d_{27} + d_{48}) & (d_{14} + d_{79}) & (d_{12} + d_{89}) \end{pmatrix} \begin{pmatrix} l^2 \\ m^2 \\ n^2 \\ mn \\ nl \\ lm \end{pmatrix}$$

Equations (9) determine the velocities of propagation of the three types of waves in any direction for crystals of the triclinic system which possess no symmetry of structure at all. The number of constants figuring in the wave equations will diminish rapidly as we pass on to crystals of higher symmetry, and become only three for crystals of the T_d , O and O_h classes. We tabulate below the wave equations for the different classes of crystals taking into account of their symmetry.

I. *Monoclinic system* (C_s, C_2, C_{2h})—*diad axis parallel to the z-axis*

$$(d_{11}l^2 + d_{88}m^2 + d_{77}n^2 + 2d_{18}lm - \rho v^2)A^x + \{d_{19}l^2 + d_{28}m^2 + d_{47}n^2 + (d_{12} + d_{89})lm\}A^y + \{(d_{38} + d_{57})mn + (d_{13} + d_{67})nl\}A^z = 0.$$

$$\{d_{19}l^2 + d_{28}m^2 + d_{47}n^2 + (d_{12} + d_{89})lm\}A^x + (d_{99}l^2 + d_{22}m^2 + d_{44}n^2 + 2d_{29}lm - \rho v^2)A^y + \{(d_{23} + d_{45})mn + (d_{39} + d_{46})nl\}A^z = 0.$$

$$\{(d_{38} + d_{57})mn + (d_{13} + d_{67})nl\}A^x + \{(d_{23} + d_{45})mn + (d_{39} + d_{46})nl\}A^y + (d_{66}l^2 + d_{55}m^2 + d_{33}n^2 + 2d_{56}lm - \rho v^2)A^z = 0.$$

The wave equations contain *twenty* independent constants.

II. *Orthorhombic system* (C_{2v}, D_2, D_{2h})

$$(d_{11}l^2 + d_{88}m^2 + d_{77}n^2 - \rho v^2)A^x + (d_{12} + d_{89})lmA^y + (d_{13} + d_{67})nlA^z = 0,$$

$$(d_{12} + d_{89})lmA^x + (d_{99}l^2 + d_{22}m^2 + d_{44}n^2 - \rho v^2)A^y + (d_{23} + d_{45})mnA^z = 0.$$

$$(d_{13} + d_{67})nlA^x + (d_{23} + d_{45})mnA^y + (d_{66}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2)A^z = 0.$$

The wave-equations involve *twelve* distinct constants.

III. *Tetragonal* (C_4, S_4, C_{4h})—*tetrad axis parallel to the z-axis*

$$\{d_{11}l^2 + d_{88}m^2 + d_{44}n^2 + 2d_{18}lm - \rho v^2\}A^x + \{d_{19}(l^2 - m^2) + (d_{12} + d_{89})lm\}A^y + \{(d_{38} - d_{46})mn + (d_{13} + d_{45})nl\}A^z = 0$$

$$\{d_{19}(l^2 - m^2) + (d_{12} + d_{89})lm\}A^x + \{d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{18}lm - \rho v^2\}A^y + \{(d_{13} + d_{45})mn + (d_{46} - d_{38})nl\}A^z = 0.$$

$$\{(d_{38} - d_{46})mn + (d_{13} + d_{45})nl\}A^x + \{(d_{13} + d_{45})mn + (d_{46} - d_{38})nl\}A^y + \{d_{55}(l^2 + m^2) + d_{33}n^2 - \rho v^2\}A^z = 0.$$

The number of independent constants contained in the wave equations is *ten*.

IV. *Tetragonal* ($C_{4v}, S_{4v}, D_4, D_{4h}$)—*tetrad axis parallel to the z-axis*

$$(d_{11}l^2 + d_{88}m^2 + d_{44}n^2 - \rho v^2)A^x + (d_{12} + d_{89})lmA^y + (d_{13} + d_{45})nlA^z = 0.$$

$$(d_{12} + d_{89})lmA^x + (d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - \rho v^2)A^y + (d_{13} + d_{45})mnA^z = 0.$$

$$(d_{13} + d_{45})nlA^x + (d_{13} + d_{45})mnA^y + \{d_{55}(l^2 + m^2) + d_{33}n^2 - \rho v^2\}A^z = 0.$$

The number of independent constants contained in the wave-equations is *seven*.

V. *Trigonal system (C₃, S₆)—triad axis parallel to the z-axis*

$$\begin{aligned} & \{d_{11}l^2 + d_{88}m^2 + d_{55}n^2 + 2d_{14}mn + 2d_{17}nl + 2d_{18}lm - \rho v^2\}A^x \\ & + \{d_{18}(m^2 - l^2) - 2d_{17}mn + 2d_{14}nl + (d_{12} + d_{89})lm\}A^y \\ & + \{d_{16}l^2 - m^2 + (d_{38} - d_{46})mn + (d_{13} + d_{45})nl + 2d_{15}lm\}A^z = 0. \end{aligned}$$

$$\begin{aligned} & \{d_{18}(m^2 - l^2) - 2d_{17}mn + 2d_{14}nl + (d_{12} + d_{89})lm\}A^x \\ & + \{d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{14}mn - 2d_{17}nl - 2d_{18}lm - \rho v^2\}A^y \\ & + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})mn + (d_{46} - d_{38})nl - 2d_{16}lm\}A^z = 0. \end{aligned}$$

$$\begin{aligned} & \{d_{16}(l^2 - m^2) + (d_{38} - d_{46})mn + (d_{13} + d_{45})nl + 2d_{15}lm\}A^x \\ & + \{d_{15}(l^2 - m^2) + (d_{13} + d_{45})mn + (d_{46} - d_{38})nl - 2d_{16}lm\}A^y \\ & + \{d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2\}A^z = 0 \end{aligned}$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89}).$$

The number of independent constants contained in the wave equations is *twelve*.

VI. *Trigonal (D₃, D_{3d}, C_{3v})—triad axis parallel to the z-axis*

$$\begin{aligned} & \{d_{11}l^2 + d_{88}m^2 + d_{55}n^2 + 2d_{14}mn - \rho v^2\}A^x + \{2d_{14}nl \\ & + (d_{12} + d_{89})lm\}A^y + \{(d_{13} + d_{45})nl + 2d_{15}lm\}A^z = 0. \end{aligned}$$

$$\begin{aligned} & \{2d_{14}nl + (d_{12} + d_{89})lm\}A^x + \{d_{88}l^2 + d_{11}m^2 + d_{44}n^2 \\ & - 2d_{14}mn - \rho v^2\}A^y + \{d_{15}(l^2 - m^2) \\ & + (d_{13} + d_{45})mn + d_{46}nl\}A^z = 0. \end{aligned}$$

$$\begin{aligned} & \{(d_{13} + d_{45})nl + 2d_{15}lm\}A^x + \{d_{15}(l^2 - m^2) \\ & + (d_{13} + d_{45})mn + d_{46}nl\}A^y + \{d_{44}l^2 + d_{55}m^2 + d_{33}n^2 \\ & - \rho v^2\}A^z = 0. \end{aligned}$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89}).$$

The number of independent constants contained in the wave equations is *eight*.

VII. Hexagonal (C_{3h} , C_6 , C_{6h})—hexad axis parallel to the z-axis

$$\{d_{11}l^2 + d_{88}m^2 + d_{55}n^2 + 2d_{18}lm - \rho v^2\}A^x + \{d_{18}(m^2 - l^2) + (d_{12} + d_{89})lm\}A^y + \{(d_{38} - d_{46})mn + (d_{13} + d_{45})nl\}A^z = 0.$$

$$\{d_{18}(m^2 - l^2) + (d_{12} + d_{89})lm\}A^x + \{d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - 2d_{18}lm - \rho v^2\}A^y + \{(d_{13} + d_{45})mn + (d_{46} - d_{38})nl\}A^z = 0.$$

$$\{(d_{38} - d_{46})mn + (d_{13} + d_{45})nl\}A^x + \{(d_{13} + d_{45})mn + (d_{46} - d_{38})nl\}A^y + \{d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2\}A^z = 0.$$

where

$$d_{88} = (d_{11} - d_{12} - d_{89}).$$

The number of independent constants contained in the wave equations is *eight*.

VIII. Hexagonal (D_{3h} , C_{6v} , D_6 , D_{6h})—hexad axis parallel to the z-axis

$$(d_{11}l^2 + d_{88}m^2 + d_{55}n^2 - \rho v^2)A^x + (d_{12} + d_{89})lmA^y + (d_{13} + d_{45})nlA^z = 0.$$

$$(d_{12} + d_{89})lmA^x + (d_{88}l^2 + d_{11}m^2 + d_{44}n^2 - \rho v^2)A^y + (d_{13} + d_{45})mnA^z = 0.$$

$$(d_{13} + d_{45})(nlA^x + mnA^y) + (d_{44}l^2 + d_{55}m^2 + d_{33}n^2 - \rho v^2)A^z = 0.$$

Here again the relation

$$d_{88} = d_{11} - d_{12} - d_{89}$$

characteristic of crystals of the trigonal systems subsists, and number of independent constants appearing in the wave equations is *six*.

IX. Cubic (T and T_h)

$$(d_{11}l^2 + d_{44}m^2 + d_{55}n^2 - \rho v^2)A^x + (d_{12} + d_{45})(lmA^y + nlA^z) = 0.$$

$$(d_{12} + d_{45})lmA^x + (d_{11}m^2 + d_{44}n^2 + d_{55}l^2 - \rho v^2)A^y + (d_{12} + d_{45})mnA^z = 0.$$

$$(d_{12} + d_{45})(nlA^x + mnA^y) + (d_{11}n^2 + d_{44}l^2 + d_{55}m^2 - \rho v^2)A^z = 0.$$

The number of independent elastic constants appearing in the wave equations is *four*.

X. Cubic (T_d , O and D_h)

$$\{d_{11}l^2 + d_{44}(m^2 + n^2) - \rho v^2\}A^x + (d_{12} + d_{45})\{(lmA^y + nlA^z)\} = 0.$$

$$(d_{12} + d_{45})lmA^x + \{d_{11}m^2 + d_{44}(l^2 + m^2) - \rho v^2\}A^y \\ + (d_{12} + d_{45})mnA^z = 0.$$

$$(d_{12} + d_{45})\{nlA^x + mnA^y\} + \{d_{11}l^2 + d_{44}(l^2 + m^2) - \rho v^2\}A^z = 0.$$

The number of independent constants appearing in the wave equations is *three*.

6. Static deformation problems

Equations (1) express the nine stress components in terms of the nine strain coefficients. One can work out the inverse transformation of (1) and express instead the strain coefficients as linear functions of the stress variables. The strain-stress relations can therefore alternatively be written also as

$$u_m = \sum_{n=1}^9 D_{mn} T_n \quad (m = 1, 2, \dots, 9) \quad (10)$$

If Δ_{mn} denotes the co-factor of the element d_{mn} in the determinant of the transformation (1) and $\Delta = \text{determinant } |d_{mn}|$, then $D_{mn} = (\Delta_{mn}/\Delta)$.

The strain-energy can be expressed purely as a function of the stress coefficients and we have another expression

$$2U = \sum_m \sum_n D_{mn} T_m T_n \quad (11)$$

for the deformation energy which is equivalent to (3).

In the classical theory the nine stress variables are reduced to six by means of the relations $T_{yz} = T_{zy}$; $T_{zx} = T_{xz}$; $T_{xy} = T_{yx}$. The deformation energy of the solid is thus a function of the six stress variables only. Adopting the usual convention of writing $T'_1, T'_2, T'_3, T'_4, T'_5, T'_6$ for $T_{xx}, T_{yy}, T_{zz}, T_{yz}$, or T_{zy}, T_{zx} or T_{xz}, T_{xy} or T_{yx} respectively, the classical expression (4) for the strain-energy becomes

$$2U_1 = \sum_m \sum_{n=1}^6 s_{mn} T'_m T'_n \quad (12)$$

The coefficients s_{mn} occurring in the above expression are the well known *elastic moduli* of the classical theory. One can obtain formulae for these moduli in terms of our constants D_{mn} by considering cases of homogeneous stresses for which the relations $T_{yz} = T_{zy}$; $T_{zx} = T_{xz}$; $T_{xy} = T_{yx}$ hold good. Making these substitutions in (11) and comparing the resulting expression with (2), we get $s_{mn} = D_{mn}$ when both m and n are 1, 2, or 3 and relations of the type

$$s_{14} = (D_{14} + D_{15}); \\ s_{44} = (D_{44} + 2D_{45} + D_{55}); \\ s_{45} = (D_{46} + D_{47} + D_{56} + D_{57}); \quad (13)$$

for the other coefficients.

We can now write down the expressions for the compressibility, Young's modulus, and the Poisson's ratio for any crystal in simple terms. In view of the fact that all these moduli are determinable from experiments dealing with purely homogeneous strains, the formulae for them are not essentially different from the corresponding ones of the classical theory. By following the same methods as those adopted in the latter³, we give below the formulae for these moduli in our present notation.

When the crystal is subjected to a uniform hydrostatic pressure P , we have from the first three of the equations (10)

$$\begin{aligned} u_1 &= (D_{11} + D_{12} + D_{13})P \\ &= (s_{11} + s_{12} + s_{13})P \quad \text{from (13)} \\ u_2 &= (s_{21} + s_{22} + s_{23})P \\ u_3 &= (s_{31} + s_{32} + s_{33})P. \end{aligned}$$

The linear compressibility modulus in the direction of the x -axis is therefore given by

$$k_x = (P/u_1) = 1/(s_{11} + s_{12} + s_{13}) \quad (14)$$

and the bulk modulus is expressed by the formula

$$k = P/(u_1 + u_2 + u_3) = 1/(s_{11} + s_{22} + s_{33} + 2s_{23} + 2s_{31} + 2s_{12}). \quad (15)$$

If the solid is subjected to a uniform tension T in the direction of the x -axis, obviously $T_1 = T$; $T_2 = T_3 = \dots T_9 = 0$. Hence it follows from (10) that the Young's modulus in the direction of the x -axis is given by

$$E = T/u_1 = (1/D_{11}) = (1/s_{11}). \quad (16)$$

Similarly the Poisson's ratio in the direction of the y -axis is given by

$$\sigma = -(s_{12}/s_{11}). \quad (17)$$

To write down the expressions for the Young's modulus and Poisson's ratio in any general direction (l, m, n) , we require the law of transformation of the strain as well as the stress components when one passes over from one co-ordinate system to another. If the direction cosines of the axes Ox' , Oy' , Oz' of a new co-ordinate system referred to the original one are $(l_1 m_1 n_1)$, $(l_2 m_2 n_2)$ and $(l_3 m_3 n_3)$ respectively, we have

$$\begin{aligned} T_{x'x'} &= l_1^2 T_{xx} + m_1^2 T_{yy} + n_1^2 T_{zz} + m_1 n_1 (T_{yz} + T_{zy}) \\ &\quad + n_1 l_1 (T_{zx} + T_{xz}) + l_1 m_1 (T_{xy} + T_{yx}) \\ T_{x'y'} &= l_1 l_2 T_{xx} + m_1 m_2 T_{yy} + n_1 n_2 T_{zz} + (m_1 n_2 T_{yz} + m_2 n_1 T_{zy}) \\ &\quad + (n_1 l_2 T_{zx} + n_2 l_1 T_{xz}) + (l_1 m_2 T_{xy} + l_2 m_1 T_{yx}) \\ T_{y'y'} &= l_1 l_2 T_{xx} + m_1 m_2 T_{yy} + n_1 n_2 T_{zz} + (m_2 n_1 T_{yz} + m_1 n_2 T_{zy}) \\ &\quad + (n_2 l_1 T_{zx} + n_1 l_2 T_{xz}) + (l_2 m_1 T_{xy} + l_1 m_2 T_{yx}) \end{aligned} \quad (18)$$

$$u_{x'x'} = l_1^2 u_{xx} + m_1^2 u_{yy} + n_1^2 u_{zz} + m_1 n_1 (u_{yz} + u_{zy}) \\ + n_1 l_1 (u_{zx} + u_{xz}) + l_1 m_1 (u_{xy} + u_{yx}) \quad (19)$$

$$u_{x'y'} = l_1 l_2 u_{xx} + m_1 m_2 u_{yy} + n_1 n_2 u_{zz} + (m_1 n_2 u_{yz} + m_2 n_1 u_{zy}) \\ + (n_1 l_2 u_{zx} + n_2 l_1 u_{xz}) + (l_1 m_2 u_{xy} + l_2 m_1 u_{yx})$$

$$u_{y'x'} = l_1 l_2 u_{xx} + m_1 m_2 u_{yy} + n_1 n_2 u_{zz} + (m_2 n_1 u_{yz} + m_1 n_2 u_{zy}) \\ + (n_2 l_1 u_{zx} + n_1 l_2 u_{xz}) + (l_2 m_1 u_{xy} + l_1 m_2 u_{yx}).$$

Now, if the solid is subjected to a uniform tension T over the planes $x' = \text{const.}$ of which the normal has direction cosines $(l_1 m_1 n_1)$, we get from the transformation rules

$$T_{xx} = l_1^2 T; \quad T_{yy} = m_1^2 T; \quad T_{zz} = n_1^2 T; \quad T_{yz} = T_{zy} = m_1 n_1 T; \\ T_{zx} = T_{xz} = n_1 l_1 T; \quad T_{xy} = T_{yx} = l_1 m_1 T.$$

Further, $u_{x'x'}$ is given by (19). Hence denoting by $\mathbf{q}_{x'}$ the row vector $(l_1^2 m_1^2 n_1^2 m_1 n_1 n_1 l_1 l_1 m_1)$ with six components, we find the expression for the Young's modulus in the direction of the vector $(l_1 m_1 n_1)$ as

$$E_{x'} = 1/\mathbf{q}_{x'} \mathbf{S} \tilde{\mathbf{q}}_{x'} \quad (20)$$

where \mathbf{S} denotes the matrix (s_{mn}) . Similarly the Poisson's ratio in the direction of the y' -axis which has direction cosines $(l_2 m_2 n_2)$ with respect to O_x , O_y and O_z is given by

$$\sigma_{y'} = -\frac{1}{2\phi} \left[l_2^2 \frac{\partial \phi}{\partial l_1^2} + m_2^2 \frac{\partial \phi}{\partial m_1^2} + n_2^2 \frac{\partial \phi}{\partial n_1^2} + m_2 n_2 \frac{\partial \phi}{\partial (m_1 n_1)} \right. \\ \left. + n_2 l_2 \frac{\partial \phi}{\partial (n_1 l_1)} + l_2 m_2 \frac{\partial \phi}{\partial (l_1 m_1)} \right] \quad (21)$$

where $\phi = \mathbf{q}_{x'} \mathbf{S} \tilde{\mathbf{q}}_{x'}$ and the differential coefficients are formed as if these arguments are independent.

It is interesting to note that only twenty-one of the forty-five constants figuring in (10) appear in the above formulae. As mentioned earlier, this is a consequence of the homogeneity of the strains applied to evaluate these static moduli.

The stresses and strains which appear when elastic materials are subject to torsion or flexure are essentially heterogeneous, and hence in dealing with them, our elastic moduli D_{mn} will appear in combinations other than those which figure in homogeneous deformations. The present theory is quite competent to handle such problems, but to deal with them in detail would carry us far beyond the scope of this paper.

7. Some concluding remarks

The main purpose of the present paper has been to establish the necessity for an amendment of the phenomenological theory of elasticity as universally accepted hitherto. Any theory to be acceptable should include in its scope elastic stresses and strains of the most general type and specify them in an analytical form from which the equations of equilibrium in static problems and the equations of motion in wave-propagation can be written down immediately. These requirements are not met by the present form of the theory but are completely satisfied if all the nine components of stress and strain in the usual tensor formulation are retained. When thus amended, the phenomenological theory is capable of handling all the problems of the subject, including those which arise in its practical applications. The more important of these are considered in detail in the course of the paper and the results are set out explicitly for the different crystal classes so that they could be readily made use of.

As already remarked in the introduction, the phenomenological theory as amended gives results in complete accord with those derived from the atomistic approach to the theory of elasticity of crystals based on the most general scheme of interatomic forces. To discuss the latter further or to give an account of the somewhat confused history of the subject would lie outside the scope of the present paper. A few remarks regarding these matters will however be found in the attached appendix.

Summary

The fundamental aspects of the phenomenological theory of elasticity are critically examined and it is shown that the tensor representation of the elastic strains and stresses in the general case should be in the unsymmetrical form. On this basis, the stress-strain relationships are deduced and tabulated for the different crystal classes. The equations determining the velocities of wave-propagation in different directions are also obtained and tabulated. Static deformation problems are then discussed and it is shown that in the particular case of homogeneous strains, the elastic constants group themselves in linear combinations which are equivalent to the elastic moduli of the theory in its familiar form. In wave-propagation, however, the strains and stresses are heterogeneous and hence all the elastic constants are involved and appear in linear combinations which are different and also larger in number than those which figure in the formulae for homogeneous deformations. These results are completely in accord with the consequences of the atomistic theory based on interatomic forces of the most general type.

Appendix

As is well known, the theory of the elasticity of solids in its present form was initiated by Cauchy who put forth the fundamental idea of expression elastic stresses and strains in the manner adopted in the phenomenological theory, and also developed the theory on an atomistic basis. Later theorists, notably Green, Stokes and Kelvin retained Cauchy's method of specifying elastic stresses and strains but adopted a purely phenomenological approach. The view advocated by them that a completely anisotropic body would have twenty-one elastic constants and not fifteen as derived by Cauchy received general acceptance.

In a paper published in these *Proceedings* some years ago by one of us (Raman, 1943), a theory of the dynamic behaviour of crystal lattices was developed based on the assumption of interatomic forces of the most general type. In subsequent years, the consequences of that theory was worked out in detail for the case of diamond and confirmed by a series of spectroscopic investigations on the scattering of light, the luminescence and infra-red absorption by that crystal. The high values of the interatomic force-constants disclosed by the spectroscopic behaviour of diamond were evidently related to its exceptional elastic behaviour. In the endeavour to place this relationship on a quantitative basis, a fresh approach was made by one of us (Viswanathan, 1954) to the atomistic theory of the elasticity of crystals, both from the static and dynamic points of view, and some surprising results emerged. Contrary to the assertion made in the papers of Max Born and his collaborators which also finds a place in their recent book (Born and Kun Huang, 1954), no difficulty was encountered in expressing the energy of static deformations in terms of interatomic forces of the most general type. It was found that this expression contained forty-five independent constants, but for homogeneous or irrotational strains they appeared in twenty-one distinct linear combinations. The dynamics of wave-propagation in crystals was also investigated and it was shown that the expressions for the wave-velocity contained the same forty-five constants but in different linear combinations. The work of Born and his school on the dynamic problem was critically examined and it was shown that the assumptions made by them in the attempt to reduce the forty-five constants which appeared in their theory to twenty-one had no theoretical justification.

The results of Born and his school were also contradicted by Laval in some recent publications (1951). More recently still, a series of papers have been published by Le Corre in which Laval's ideas have been further developed. On reading those papers, one obtains the impression that their author believes the results of the atomistic and phenomenological approaches to differ essentially. For example, in order to account for the non-symmetric character of the stress tensor, internal couples are postulated to balance the differences in the angular momenta. We may remark that there is no room for such a postulate, since the analytical specification of the stresses in terms of the tensor components should

itself suffice to describe the state of the solid completely. In the last paper of the series, a statement also appears that an atomistic approach is essential to solve such familiar problems in elasticity as torsion and flexure.

In conclusion, we have to thank Mr A K Ramdas for his help in the preparation of the tables appearing in the paper.

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Evaluation of the four elastic constants of some cubic crystals

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1. Introduction

The mathematical theory of elasticity in its generally accepted form derives from a memoir by A L Cauchy presented to the Academy of Sciences at Paris in 1822. The analytical specification of the strains and stresses in elastic solids adopted in that theory expresses the strains in terms of the differential displacements of neighbouring points in the solid and the stresses in terms of the tractive forces on infinitesimal areas in the same location. The theory, however, does not make use of these representations with complete generality, but following Cauchy, adopts them in modified forms on the basis of arguments put forward by him and considered as authoritative ever since. But when one examines those arguments critically, they are found to be indefensible. This is particularly clear in regard to the representation of strains. In the most general case, we have nine components of strain, but Cauchy reduced their number to six by eliminating movements which he identified with rigid body rotations. Actually, however, the components thus eliminated are not rigid body rotations, but differential rotations which are of the same nature as those appearing in the deformation of solids by torsion or flexure and hence, their elimination is not justified. Then again, Cauchy's reduction in the number of the stress components from nine to six is based on the idea that the angular momenta of the tractions taken about each of the coordinate axes and summed up should cancel out. But since the stresses are assumed to be in the nature of tractive forces and defined in terms of their magnitudes over infinitesimal areas, they have to be considered as acting on volume elements which are small enough to be regarded as particles and hence no consideration of angular momenta is called for. The reduction in number of the components of stress from nine to six has therefore no justification. Indeed, when once it is admitted that we have to retain all the nine components of strain, a similar step in regard to the components of stress follows inevitably.

In a recent paper (Raman and Viswanathan, 1955) the consequences of adopting the representations of stress and strain in elastic solids in their most

general form have been discussed in detail. It has been shown in that paper that Cauchy's assumptions result in restricting the cases which fall within its scope to homogeneous strains properly-so-called. The more general case of heterogeneous strains, including especially all cases of wave-propagation and static deformations in the nature of torsion and flexure, lie outside its scope. Nevertheless, the mathematical theory of elasticity has actually been applied to these cases and formulae have been obtained and the constants appearing in them have been evaluated experimentally. For example, the results of experimental studies with cubic crystals have been expressed in terms of three constants usually designated as C_{11} , C_{12} and C_{44} respectively. On the other hand, the more general theory shows that four constants designated as d_{11} , d_{12} , d_{44} and d_{45} are needed for the classes Oh and Td of the cubic system. Hence, by an examination of the experimental data for those cubic crystals of the Oh and Td classes which have been investigated with adequate precision by different methods, it should be possible to decide whether those data are expressible in terms of three constants only, or whether four constants are actually needed. It is the object of the present paper to present the results of such an examination.

2. Some general remarks

The determination of elastic constants of crystals can be made independently by static and dynamic methods. In the former case we naturally deal with the elastic constants under isothermal conditions and in the latter case under adiabatic conditions. The dynamic methods depend upon the determination of velocity of propagation of high-frequency waves of different types in the solid. Many of the recent determinations of the elastic constants of crystals have been made by these methods and it would seem that a high degree of precision has been attained in the resulting data. We shall accordingly make use of them in the evaluation of the elastic constants of the respective materials.

The classical expression for the velocity of propagation in a cubic crystal in the older theory is given by equations of the type

$$\rho v^2 A^x = A^x \{C_{11} l^2 + C_{44} (m^2 + n^2)\} + (C_{12} + C_{44})(A^y l m + A^z l n)$$

while in the corrected theory it is given by equations of the type

$$\rho v^2 A^x = A^x \{d_{11} l^2 + d_{44} (m^2 + n^2)\} + (d_{12} + d_{45})(A^y l m + A^z l n).$$

Thus in reducing the experimental data we make the following identifications:

$$d_{11} = C_{11}; \quad d_{44} = C_{44} \quad \text{and} \quad (d_{12} + d_{45}) = (C_{12} + C_{44}).$$

It will be seen at once that if $d_{44} = d_{45}$, then the two theories lead to identical results.

Whereas in the older theory, if the wave-velocities had been measured for a sufficient number of directions the data resulting would suffice to determine the constants C_{11} , C_{12} and C_{44} , in the present theory it only enables us to evaluate the three quantities d_{11} , d_{44} and $(d_{12} + d_{45})$. Thus, at least one additional determination is needed by static methods yielding values for a different linear combination of the four constants. The most appropriate determination appears to be the bulk modulus the expression for which under the older theory is $(C_{11} + 2C_{12})/3$, whereas in the new theory it is $(d_{11} + 2d_{12})/3$. While determinations of the bulk modulus are not easy, there is reason to believe that a degree of precision adequate for our present purpose has been reached in the measurements made and reported from Bridgman's laboratory at Harvard. It is obvious that to utilize these data in conjunction with the determinations by the dynamic methods, it is necessary to assume that we are dealing in both cases with the same material and under the same physical conditions. Such an assumption would appear *prima facie* justifiable in the cases considered in the present paper, viz., crystallised solids of very simple chemical composition. The correctness of the assumption is reinforced by an intercomparison of the elastic constants determined by dynamic methods and reported by different authors from different laboratories. In general, these values do not differ more than can reasonably be ascribed to inevitable uncertainties in the experimental determinations.

Some further remarks are also necessary in this connection. Since the experimental values for the compressibility refer to isothermal conditions it is necessary to correct them to obtain its value under adiabatic conditions in order that a comparison might be possible with the adiabatic constants determined by dynamic methods. This correction is effected making use of the well known formula

$$\chi_{\text{iso}} - \chi_{\text{adia}} = \frac{9\alpha^2 T}{\rho C_p}$$

where χ represents the compressibility, α the coefficient of linear expansion of the substance, T the absolute temperature, ρ the specific gravity of the solid and C_p the specific heat of the solid in ergs per gram. The numerical values of the constants used in the calculation of this correction term have been taken from the *Landolt-Bornstein Tables* and the *International Critical Tables*.

The compressibility determinations made in Bridgman's laboratory usually extended upto very high pressures. We naturally make use of the compressibility value for zero pressures computed by the investigators themselves from the experimental data. The values reported by Bridgman and Slater prior to 1946 are subject to correction by a constant term $-0.033 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ in the light of Bridgman's latest determination of the linear compressibility of iron. Since the compressibility as well as the other elastic constants are functions of temperature, it is necessary that the comparison should be made for their values at the same temperature, either as reported by the authors themselves or as reduced to the

same temperature from a knowledge of the variation of the elastic constants with temperature.

In selecting the substances the data for which are discussed in the present paper, the choice has naturally fallen on those substances which have been frequently the subject of experimental study. It so happens that these substances also fall into well-defined groups being very similar in chemical composition and their crystal structure, e.g., NaCl, KCl, KBr, NaBr, LiF, MgO and AgCl, all of which have the rock-salt structure; diamond, silicon, germanium, zinc blende and fluorspar all of which again have closely similar structures and finally the metallic elements aluminium, copper, nickel and silver which have the face-centred cubic structure. In tabulating our final results we have arranged the substances in the order stated, in order to facilitate intercomparison of their elastic behaviour.

3. Crystals with the rock-salt structure

(a) *Rock-salt*—The elastic constants of NaCl were determined by Voigt first in 1888 by the methods of torsion and flexure. Bridgman has also in 1929 determined the constants by the same methods. With the development of techniques based on ultrasonic wave-propagation, several determinations have been made recently by numerous investigators namely, Bergmann, Rose, Durand, Hunter and Siegel, Huntington, Galt, Lazarus and Bhagavantam. The values reported by these investigators and the methods used by them are given in table 1.

The values for C_{12} reported by the investigators who have used the static methods are distinctly higher than the values for the same constant obtained using dynamic methods, and this difference appears to be larger than can be reasonably ascribed to experimental errors. On the other hand, the values for C_{11} and C_{44} do not exhibit such a difference. The close agreement between the results

Table 1

Author	Method	C_{11}	C_{12}	C_{44}
Voigt	Static	4.77	1.32	1.29
Bridgman	"	4.94	1.37	1.28
Bergmann	Diffraction patterns	4.77	1.25	1.21
Rose (270° K)	Composite oscillator	5.06	1.30	1.278
Durand (300° K)	"	4.96	1.31	1.268
Hunter and Siegel	"	4.86	1.194	1.281
Huntington (25° C)	Pulse	4.85	1.23	1.265
Galt (298° K)	"	4.87	1.24	1.260
Lazarus (298° K)	"	4.911	1.225	1.284
Bhagavantam (R.T.)	Ultrasonic	4.97	1.27	1.27

reported by the three investigators who have used the pulse technique indicate that this method yields precise results. Hence, the mean of the values reported by these three workers have been adopted here as the best values.

The isothermal compressibility had been determined by static methods by a series of investigators, viz., Rontgen and Schneider, Madelung and Fuchs, Richards and Jones, Adams, Williamson and Johnston, Slater and Bridgman. Table 2 shows the values reported by the various authors. Of these, the most accurate are evidently those reported by Slater and Bridgman, and they have accordingly been adopted as correct. The values reported by Madelung and Fuchs refer to the pressure range 50–200 kg/cm², those of Richards and Jones to the range 100–510 kg/cm². The values of Slater and Bridgman quoted are for zero pressure always.

Table 2

Author	Temp.	χ in $10^{-7} \text{ kg}^{-1} \text{ cm}^2$
Rontgen and Schneider	R.T.	50
Madelung and Fuchs	0° C	40.5
Richards and Jones	20° C	44.0
Adams, Williamson and Johnston	R.T.	40.4
Slater	30° C	41.8
Bridgman	30° C	41.82
	75° C	43.44

These values are however subject to correction by a constant term $-0.033 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ in the light of Bridgman's latest determination of the linear compressibility of iron. After making this correction and using the known value of g at Harvard, the isothermal compressibility of rock-salt comes out as $42.62 \times 10^{-13} \text{ cm}^2/\text{dyne}$ at 30° C. The value of the compressibility at 25° C is found by linear interpolation from the values reported by him at 30° C and 75° C. This correction when effected leads to a value of χ (isothermal) = 42.44. The difference between the isothermal and adiabatic compressibilities can be calculated from the formula given earlier. For rock-salt, the numerical values used in the formula are: $\alpha = 44 \times 10^{-6}$; $\rho = 2.168$; $C_p = 0.2078 \text{ cal/gm}$. The value of the adiabatic compressibility at 25° C is found to be $39.68 \times 10^{-13} \text{ cm}^2/\text{dyne}$. Hence the bulk modulus comes out as $2.52 \times 10^{11} \text{ dynes/cm}^2$. On the other hand, the value for the bulk modulus calculated from the formula $(C_{11} + 2C_{12})/3$ comes out at $2.45 \times 10^{11} \text{ dynes/cm}^2$ the difference clearly being greater than can be explained in terms of experimental errors. The average values of the dynamically determined constants used in the calculation are: $C_{11} = 4.877$; $C_{12} = 1.232$; $C_{44} = 1.269 \times 10^{11} \text{ dynes/cm}^2$, while the four constants evaluated in the manner already explained come out as $d_{11} = 4.88$; $d_{12} = 1.34$; $d_{44} = 1.27$; and $d_{45} = 1.16 \times 10^{11} \text{ dynes/cm}^2$.

(b) *Potassium chloride*—The elastic constants of KCl have been determined by static methods by Voigt, Forsterling and Bridgman. The later workers who have determined the elastic constants by the dynamic methods of ultrasonics are Durand, Galt and recently Lazarus. Their values appear in table 3.

It will be noticed from table 3 that the values reported by the different authors are in much less satisfactory agreement amongst themselves than in the case of rock-salt. The values for C_{12} in particular appear rather erratic and this is probably due to the fact that measurements usually involve the determination of linear combinations of C_{11} and C_{12} and since C_{12} is much smaller of the two, errors of measurement would influence its determined value very noticeably. Voigt gives C_{12} to three significant figures but his value is undoubtedly an error. As in the case of rock-salt we shall assume as a definitive value the mean of the measurements by the pulse method at 25° C.

Table 3

Author		Method	C_{11}	C_{12}	C_{44}
Voigt	R.T.	Static	3.75	0.198	0.655
Forsterling	R.T.	"	3.88	0.640	0.65
Bridgman	30° C	"	3.70	0.81	0.79
Durand	R.T.	Composite oscillator	4.00	0.6	0.625
Galt	25° C	Pulse	3.98	0.625	0.62
Lazarus	25° C	"	4.095	0.705	0.630

The static measurements of compressibilities by different authors shown in table 4 agree remarkably well amongst themselves. We shall here accept the measurement by Slater as corrected by Bridgman to be the most reliable. This comes out as 56.27×10^{-13} dynes⁻¹ cm² at 30° C and after correction using the temperature coefficient given by Slater, the value at 25° C is found as 56.14×10^{-13} cm²/dyne. From this the adiabatic compressibility at 25° C is calculated using the following values for KCl in the correction formula.

Table 4

Author	Temp.	χ in 10^{-7} kg ⁻¹ cm ²
Röntgen and Schneider	—	56
Madelung and Fuchs	0° C	55.1
Richards and Jones	20° C	53.0
Slater	30° C	55.2

$\alpha = 36 \times 10^{-6}$; $\rho = 1.992$; and $C_p = 0.1661$ cal/gm. The adiabatic compressibility is found to have a value 53.62×10^{-13} . Hence the bulk modulus at 25°C comes out as 1.865×10^{11} dynes/cm².

The mean values for C_{11} , C_{12} and C_{44} adopted are 4.038, 0.663 and 0.628×10^{11} respectively. The bulk-modulus calculated using the classical expression $(C_{11} + 2C_{12})/3$ comes out as 1.788×10^{11} dynes/cm², which is definitely smaller than the experimentally determined value. The values found for the four elastic constants of the new theory are respectively: $d_{11} = 4.038$; $d_{12} = 0.799$; $d_{44} = 0.628$; $d_{45} = 0.512 \times 10^{11}$ dynes/cm².

(c) *Potassium bromide*—Static measurements of the elastic constants have been reported by Bridgman. Using the pulse technique Huntington and Galt have independently determined the constants at room temperature. The values are given in table 5.

Table 5

Author		Method	C_{11}	C_{12} $\times 10^{11}$ dynes/cm ²	C_{44}
Bridgman	30°C	Static	3.33	0.58	0.62
Huntington	25°C	Pulse	3.45	0.54	0.508
Galt	25°C	"	3.46	0.58	0.505

The compressibility measurements have been made by Richards and Jones, and Slater independently and the values reported are 6.5×10^{-6} kg⁻¹ cm² at 20°C and 6.57×10^{-6} kg⁻¹ cm² at 30°C respectively, being in good agreement with each other. Using the temperature coefficient given by Slater, the isothermal compressibility at 25°C on calculation is found to be 66.78×10^{-13} cm² dyne⁻¹. The adiabatic compressibility is found using the correction formula given earlier. The values adopted for KBr are: $\alpha = 41 \times 10^{-6}$; $\rho = 2.756$; $C_p = 0.1033$ cal./gm. $\chi_{(\text{adiabatic})}$ comes out as 62.99×10^{-13} cm²/dyne and hence the bulk modulus is 1.588×10^{11} dynes/cm² at 25°C .

Adopting the mean of the values given by Galt and Huntington the bulk modulus in terms of the classical formula $(C_{11} + 2C_{12})/3$ is found to be 1.525×10^{11} dynes/cm², thus differing from the actually observed value corrected for the adiabatic nature of deformation.

The values adopted for the elastic constants are $C_{11} = 3.455$, $C_{12} = 0.56$, $C_{44} = 0.507$, while the four constants evaluated in the manner explained are $d_{11} = 3.455$; $d_{12} = 0.655$; $d_{44} = 0.507$; $d_{45} = 0.412 \times 10^{11}$ dynes/cm².

(d) *Sodium bromide*—The static measurements of the elastic constants are due to Bridgman, while they have been determined by Bhagavantam using ultrasonic methods.

Table 6

Author	Temp.	C_{11}	C_{12}	C_{44}
Bridgman	30° C	3.30	1.31	1.33
Bhagavantam	R.T.	3.87	0.97	0.97

The values reported by Bhagavantam differ appreciably from those of Bridgman. However, we shall take for our calculations the values determined by dynamic methods as usual, since the identification of the constants of the new theory with that of the older theory is by identifying the two wave-equations.

The compressibility determinations in the case of NaBr have been made by Richards and Saerens at 20° C, the value being $5.4 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$ in the pressure range 100–510 kg/cm^2 , and by Slater at 30° C who reports a zero pressure value of $4.98 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2$. The isothermal compressibility at 30° C is found to be $50.762 \times 10^{-13} \text{ cm}^2/\text{dyne}$. Correcting this to the adiabatic value we get $\chi_{(\text{adiabatic})}$ as 47.576. The values used in the calculation of the correction term are: $\alpha = 43 \times 10^{-6}$; $\rho = 3.213$; $C_p = 0.1178 \text{ cal/gm}$. The bulk modulus value hence comes out as $2.102 \times 10^{11} \text{ dynes/cm}^2$ whereas according to the classical theory this value should be $1.936 \times 10^{11} \text{ dynes/cm}^2$.

The values of the elastic constants according to the new theory are: $d_{11} = 3.87$; $d_{12} = 1.22$; $d_{44} = 0.97$; $d_{45} = 0.72 \times 10^{11} \text{ dynes/cm}^2$.

(e) *Lithium fluoride*—The elastic constants of LiF have been determined by dynamic methods by Bergmann, Huntington, Sundara Rao and Seshagiri Rao and their values are shown in table 7.

Table 7

Author	Temp.	Method	C_{11}	C_{12}	C_{44}
Bergman	R.T.	Diffraction patterns	12.0	4.41	6.4
Huntington	25° C	Pulse	9.74	4.04	5.54
Sundara Rao	R.T.	Ultrasonic	11.9	4.58	5.42
Seshagiri Rao	R.T.	"	11.9	5.38	5.34

It will be noticed that there are notable divergences between the values reported by different investigators though they all use ultrasonic methods. A clue to the origin of these differences is to be found in the differences in density reported by the different investigators in their respective papers. The density of

LiF calculated from the lattice spacing and known atomic weights is 2.627, while Huntington, Seshagiri Rao and Sundara Rao give the density as 2.295, 2.635 and 2.601 respectively. The value found in Landolt Bornstein Table is 2.640. As the value reported by Seshagiri Rao corresponds to this, we use his data in our calculations.

The compressibility of LiF has been determined by Slater as $15.3 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ at 30° C and in a redetermination Bridgman has corrected this value and gives it as $14.95 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$. The isothermal compressibility at 30° C is accordingly $15.215 \times 10^{-13} \text{ cm}^2 \text{ dyne}^{-1}$. The following values are used in the correction term for adiabatic compressibility; $\alpha = 36 \times 10^{-6}$; $\rho = 2.64$; and $C_p = 0.373 \text{ cal/gm}$. The adiabatic compressibility comes out as 14.357×10^{-13} and hence the bulk modulus as $6.965 \times 10^{11} \text{ dynes/cm}^2$, while the bulk modulus using the data of Seshagiri Rao and the classical formula $(C_{11} + 2C_{12})/3$ is found to be having a different value of $7.55 \times 10^{11} \text{ dynes/cm}^2$. Using the values of Seshagiri Rao in our calculation we find the following values for the four elastic constants. $d_{11} = 11.9$; $d_{12} = 4.5$; $d_{44} = 5.34$; and $d_{45} = 6.22 \times 10^{11} \text{ dynes/cm}^2$.

(f) *Magnesium oxide*—The elastic constants of MgO have been determined dynamically by Durand and by Bhagavantam and their values are shown below.

Table 8

Author		C_{11}	C_{12}	C_{44}
Durand	30° C	28.92	8.77	14.47
Bhagavaniam	R.T.	28.6	8.7	14.8

Their values agree fairly well and the slight difference in the value of C_{44} might be due to experimental errors. No static determinations of the elastic constants appear to have been made.

The compressibility of MgO has been determined by Madelung and Fuchs and by Bridgman. The former investigators report varying values with the different specimens they used, while Bridgman using a clear single crystal has reported the value of $5.904 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ at 30° C . The isothermal compressibility at 30° C is hence $5.988 \times 10^{-13} \text{ cm}^2/\text{dyne}$. The values of the constants appearing in the correction term are: $\alpha = 13.3 \times 10^{-6}$; $\rho = 3.576$; $C_p = 0.2297 \text{ cal/gm}$. The adiabatic compressibility comes out as 5.847×10^{-13} and hence the bulk modulus as $17.10 \times 10^{11} \text{ dynes/cm}^2$.

We shall make use of the mean of the two dynamic determinations for the purposes of our calculation, i.e., $C_{11} = 28.76$; $C_{12} = 8.74$ and $C_{44} = 15.14$. The compressibility calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be equal to $15.41 \times 10^{11} \text{ dynes/cm}^2$, being distinctly different from the observed and corrected value of 17.10×10^{11} . The elastic constants according to the new theory

are as follows: $d_{11} = 28.76$; $d_{12} = 11.27$; $d_{44} = 15.14$; $d_{45} = 12.61 \times 10^{11}$ dynes/cm².

(g) *Silver chloride*—The elastic constants of AgCl have been recently determined using the pulse method by Arenberg (1950). The values have been reported for two different specimens and show good agreement between themselves. However, it is stated by him that the values from one of the specimens are to be preferred and they are given as $C_{11} = 6.05$; $C_{12} = 3.64$; $C_{44} = 0.624 \times 10^{11}$ dynes/cm². The compressibility of fused and solidified AgCl has been determined by Richards and Jones, while Bridgman has studied the case of AgCl with compressed powder. The isothermal bulk-modulus value of 4.12×10^{11} obtained by extrapolating Bridgman's data to zero pressure agrees well with the value of 4.17×10^{11} dynes/cm² reported by Richards and Jones. Adopting the value due to Bridgman and using the values $\alpha = 30 \times 10^{-6}$; $\rho = 5.5$; and $C_p = 0.0875$ cal/gm. for AgCl, the adiabatic bulk modulus is found to be 4.338×10^{11} dynes/cm². According to the classical formula $(C_{11} + 2C_{12})/3$ this value comes out as 4.444×10^{11} dynes/cm², being different from the value given above. The four elastic constants according to the new theory are: $d_{11} = 6.05$; $d_{12} = 3.482$; $d_{44} = 0.624$; $d_{45} = 0.782 \times 10^{11}$ dynes/cm².

4. Crystals with the diamond-like structure

(a) *Diamond*—The elastic constants of diamond have been determined by the ultrasonic wedge method by Bhagavantam and Bhimasenachar (1946). The following are the values reported by them. $C_{11} = 9.5 \times 10^{12}$; $C_{12} = 3.9 \times 10^{12}$ and $C_{44} = 4.3 \times 10^{12}$ dynes/cm². The compressibility has been determined first by Adams and again by Williamson in the same laboratory, the values being 0.16×10^{-12} and 0.18×10^{-12} cm²/dyne respectively. The latter value is reported to be preferred since better material was used in the determination by Williamson. This gives a value of 5.56×10^{12} dynes/cm² for the isothermal bulk modulus. The correction for the adiabatic bulk modulus is negligible. Using this value of 5.56×10^{12} and the reported values for the elastic constants the values of the four elastic constants are calculated. They are: $d_{11} = 9.5$; $d_{12} = 3.59$; $d_{44} = 4.30$; and $d_{45} = 4.61 \times 10^{12}$ dynes/cm².

(b) *Germanium*—The elastic constants of Ge have been determined by ultrasonic methods by Bond and others, Fine and McSkimin and their values are shown in table 9.

All the determinations have been made in the Bell Telephone Laboratories and McSkimin and Fine have studied the variations of the constants with temperature. The values show good agreement between themselves. The values due to

Table 9

Author		Method	C_{11}	C_{12}	C_{44}
Bond and others	25°C	Pulse	12.90	4.84	6.69
Fine	25°C	Composite oscillator	13.16	5.09	6.69
McSkimin	30°C	Pulse	12.88	4.825	6.705

McSkimin are taken from the graphs given by him exhibiting the variation of the elastic constants with temperature.

The compressibility of *polycrystalline* germanium has been determined by Bridgman at 30° C on two occasions with different specimens and the values are $13.78 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ and $14.11 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ and the latter value is said to be more reliable. The isothermal compressibility at 30° C is hence $14.358 \times 10^{-13} \text{ cm}^2/\text{dyne}$. The constants used in the correction term to find the adiabatic compressibility are: $\alpha = 5.5 \times 10^{-6}$; $\rho = 5.323$; $C_p = 22.3 \text{ Joules/gm atom}$. The corrected value of the adiabatic compressibility is $14.308 \times 10^{-13} \text{ cm}^2/\text{dyne}$ and hence the bulk modulus value is $6.989 \times 10^{11} \text{ dynes/cm}^2$.

The elastic constants for 30° C could be more accurately and directly obtained from McSkimin's detailed data. Using his values we find that the bulk modulus value according to the classical formula should be $7.51 \times 10^{11} \text{ dynes/cm}^2$. The four elastic constants are found to be $d_{11} = 12.88$; $d_{12} = 4.04$; $d_{44} = 6.705$; and $d_{45} = 7.49 \times 10^{11} \text{ dynes/cm}^2$.

(c) *Silicon*—The elastic constants of crystalline silicon have been determined by McSkimin and others and subsequently in detail by McSkimin over a wide range of temperatures. The following values for the constants at 30° C are found from the graphs given by him. $C_{11} = 16.56$; $C_{12} = 6.386$; $C_{44} = 7.953 \times 10^{11} \text{ dynes/cm}^2$. The compressibility of *polycrystalline* silicon has been determined over a wide range of pressures by Bridgman at 30° C and on extrapolating his values to zero pressure, the isothermal compressibility is found to be $9.92 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$, i.e., $10.118 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$. The following values are used in the correction term for adiabatic compressibility. $\alpha = 2.25 \times 10^{-6}$; $\rho = 2.331$; $C_p = 0.1712 \text{ cal/gm}$. On correction the adiabatic compressibility is found to be $10.11 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$ and hence the bulk modulus as $9.89 \times 10^{11} \text{ dynes/cm}^2$. The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $9.78 \times 10^{11} \text{ dynes/cm}^2$. The four elastic constants calculated are: $d_{11} = 16.56$; $d_{12} = 6.56$; $d_{44} = 7.953$; and $d_{45} = 7.78 \times 10^{11} \text{ dynes/cm}^2$.

(d) *Zinc blende*—The elastic constants of zinc blende have been reported by Bhagavantam and Suryanarayana using ultrasonic methods. The constant C_{44} has however been obtained by them from static torsion experiments. The crystalline material used by them contained only 94% of zinc sulphide. The

following values are reported by them. $C_{11} = 10.79 \times 10^{11}$; $C_{12} = 7.22 \times 10^{11}$; $C_{44} = 4.12 \times 10^{11}$. These values are in disagreement with the values reported by Voigt from static methods, which are: $C_{11} = 9.43 \times 10^{11}$; $C_{12} = 5.68 \times 10^{11}$; $C_{44} = 4.37 \times 10^{11}$.

The compressibility of a single crystal of zinc blende has been determined by Bridgman as $12.81 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ at 30°C . This gives a value of $13.032 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$ at 30°C for the isothermal compressibility. The constants used in the correction term for adiabatic compressibility are: $\alpha = 6.7 \times 10^{-6}$; $\rho = 4.102$; and $C_p = 0.1146 \text{ cal/gm}$. The corrected value of the adiabatic compressibility is found to be $12.97 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$, and hence the bulk modulus is $7.71 \times 10^{11} \text{ dynes/cm}^2$. The bulk-modulus calculated from the formula $(C_{11} + 2C_{12})/3$ using Bhagavantam and Suryanarayana's values is 8.41×10^{11} whereas Voigt's values give $6.93 \times 10^{11} \text{ dynes/cm}^2$.

In the calculation of the four elastic constants, we make use of Bhagavantam and Suryanarayana's values since they are for the major part obtained from dynamic methods. We obtain the following values for the constants. $d_{11} = 10.79$; $d_{12} = 6.17$; $d_{44} = 4.12$; and $d_{45} = 5.17 \times 10^{11} \text{ dynes/cm}^2$.

(e) *Fluorspar*—The elastic constants of fluorspar have been determined using static methods by Voigt, and by Bergmann and Bhagavantam using dynamic methods. Their values are shown in table 10.

Table 10

Author	Method	C_{11}	C_{12}	C_{44}
Voigt	Static	16.4	4.47	3.38
Bergmann	Diffraction patterns	16.76	4.72	3.69
Bhagavantam	Ultrasonic	16.44	5.02	3.47

For our calculations we take here the mean of the values of Bergmann and Bhagavantam, i.e., $C_{11} = 16.6$; $C_{12} = 4.87$; and $C_{44} = 3.58 \times 10^{11} \text{ dynes/cm}^2$.

The compressibility of CaF_2 has been determined by Madelung and Fuchs at 0°C and in the pressure range $50\text{--}200 \text{ kg/cm}^2$ and the value reported by them is $12.2 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$. Bridgman has also determined the compressibility at 30°C and reports a zero pressure value of $12.06 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$, i.e., $12.267 \times 10^{-13} \text{ cm}^2/\text{dyne}$. The values used in the correction term are: $\alpha = 19.11 \times 10^{-6}$; $\rho = 3.18$; $C_p = 0.887 \text{ Joules/gm}$. The adiabatic compressibility value is found to be $11.914 \times 10^{-13} \text{ cm}^2/\text{dyne}$ and hence the bulk modulus is $8.39 \times 10^{11} \text{ dynes/cm}^2$. The bulk modulus value using the formula $(C_{11} + 2C_{12})/3$ is found to be $8.78 \times 10^{11} \text{ dynes/cm}^2$.

The four elastic constants calculated are: $d_{11} = 16.6$; $d_{12} = 4.29$; $d_{44} = 3.58$; and $d_{45} = 4.16 \times 10^{11} \text{ dynes/cm}^2$.

5. Metals crystallizing in the cubic system

(a) *Aluminium*—The elastic constants of single crystals of aluminium have been determined using static methods of Goens. Recently Lazarus and Sutton have independently measured the elastic constants by ultrasonic methods. The values reported by all these investigators are shown in table 11.

The accuracy in the measurements of Lazarus is greater than that of Sutton as is evidenced by the comments made by them in their respective papers. Moreover the purity of the specimens used by Lazarus and Sutton is given as 99.99% and 99.93% respectively. In view of these facts we take Lazarus's values for the purposes of our calculation.

Table 11

Author	Method		C_{11}	C_{12}	C_{44}
Goens	R.T.	Static	10.82	6.22	2.84
Lazarus	25° C	Pulse	10.56	6.39	2.853
Sutton	20° C	Composite oscillator	11.29	6.65	2.783

The isothermal compressibility of aluminium single crystals has been determined by Bridgman as $13.38 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ at 30° C and as $13.76 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ at 75° C. The value at 25° C on linear extrapolation comes out as $13.338 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$, i.e., $13.57 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$. The following values for the constants are used in the correction term for adiabatic compressibility: $\alpha = 23.06 \times 10^{-6}$; $\rho = 2.702$; $C_p = 0.2129 \text{ cal/gm}$. The adiabatic compressibility is found to be $12.97 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$ and hence the bulk modulus is $7.71 \times 10^{11} \text{ dynes/cm}^2$. The bulk modulus obtained from the values of Lazarus is 7.78×10^{11} . The values of the four elastic constants calculated are: $d_{11} = 10.56$; $d_{12} = 6.29$; $d_{44} = 2.853$; $d_{45} = 2.953 \times 10^{11} \text{ dynes/cm}^2$.

(b) *Copper*—The elastic constants of copper single crystals have been determined using the composite oscillator method by Goens and Weerts. Recently Lazarus, Long, and Overton and Gaffney have determined the constants using pulse methods. The values are shown in table 12.

Table 12

Author	Method		C_{11}	C_{12}	C_{44}
Goens and Weerts	R.T.	Composite oscillator	16.98	12.26	7.53
Lazarus	25° C	Pulse	17.1	12.39	7.56
Long	300° K	"	16.83	12.21	7.54
Overton and Gaffney	300° K	"	16.84	12.14	7.54

There is very good agreement between the three sets of values determined by the pulse method and hence for the purposes of our calculation we shall make use of the mean of these values.

The compressibility of polycrystalline copper of high purity has been determined by Bridgman as $7.19 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ at 30° C and 7.34×10^{-7} at 75° C . Hence the value at 300° K is found to be $7.173 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$, i.e., $7.283 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$. The following values are used in the correction term for the adiabatic compressibility: $\alpha = 17.09 \times 10^{-6}$; $\rho = 8.92$; $C_p = 0.0919 \text{ cal/gm}$. The corrected value of adiabatic compressibility is $7.05 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$ and hence the bulk modulus is $14.18 \times 10^{11} \text{ dynes/cm}^2$. The average values of the elastic constants from pulse method are: $C_{11} = 16.92$; $C_{12} = 12.25$ and $C_{44} = 7.55 \times 10^{11} \text{ dynes/cm}^2$. The bulk modulus using the formula $(C_{11} + 2C_{12})/3$ is found to be $13.81 \times 10^{11} \text{ dynes/cm}^2$. The four elastic constants calculated are: $d_{11} = 16.92$; $d_{12} = 12.81$; $d_{44} = 7.55$; and $d_{45} = 6.99 \times 10^{11} \text{ dynes/cm}^2$.

(c) *Nickel*—The elastic constants of single crystals of nickel have been determined recently using the ultrasonic pulse method by Bozorth and others and also by Neighbours and others. Their values are given in table 13.

Table 13

Author	C_{11}	C_{12} in $10^{12} \text{ dynes/cm}^2$	C_{44}
Bozorth and others	2.53	1.58	1.22
"	2.524	1.538	1.23
"	2.523	1.566	1.23
Neighbours and others	2.528	1.52	1.238

The average value of these at 25° C are: $C_{11} = 2.526$; $C_{12} = 1.551$; and $C_{44} = 1.23 \times 10^{12} \text{ dynes/cm}^2$.

The compressibility of pure nickel has been determined by Bridgman at 30° C as $5.29 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$ and at 75° C as 5.35×10^{-7} . The value at 25° C is hence $5.283 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$. The isothermal compressibility is hence $5.355 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$. The values used in the correction term for adiabatic compressibility are: $\alpha = 13.15 \times 10^{-6}$; $\rho = 8.9$; and $C_p = 0.107 \text{ cal/gm}$. The adiabatic compressibility is found to be $5.239 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$ and hence the bulk modulus is $19.09 \times 10^{11} \text{ dynes/cm}^2$. The bulk modulus using the classical formula is found to be $18.76 \times 10^{11} \text{ dynes/cm}^2$. The four elastic constants calculated are: $d_{11} = 25.26$; $d_{12} = 16.01$; $d_{44} = 12.3$; and $d_{45} = 11.8 \times 10^{11} \text{ dynes/cm}^2$.

(d) *Silver*—The elastic constants of single crystals of silver have been determined by Rohl using the classical static and dynamic methods. The constants have been

recently determined by Bacon and Smith using the ultrasonic pulse method. The values are shown below.

Table 14

Author		Method	C_{11}	C_{12}	C_{44}
Rohl	R.T.	Static etc.	11.9	8.94	4.37
Bacon and Smith	R.T.	Pulse	12.4	9.34	4.61

The compressibility of pure silver has been determined by Bridgman at 30° C as $9.87 \times 10^{-7} \text{ kg}^{-1} \text{ cm}^2$, i.e., $10.034 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$. The constants used in the correction term are: $\alpha = 18.9 \times 10^{-6}$; $\rho = 10.5$; $C_p = 25.2 \text{ Joules/gm atom}$. The adiabatic compressibility is found to be $9.939 \times 10^{-13} \text{ dynes}^{-1} \text{ cm}^2$ and hence the bulk modulus is $10.06 \times 10^{11} \text{ dynes/cm}^2$. The value calculated using the formula $(C_{11} + 2C_{12})/3$ is found to be $10.36 \times 10^{11} \text{ dynes/cm}^2$. The four constants calculated are: $d_{11} = 12.4$; $d_{12} = 8.89$; $d_{44} = 4.61$; and $d_{45} = 5.06 \times 10^{11} \text{ dynes/cm}^2$.

6. Some final remarks

In table 15 the results for the individual cases given in the foregoing pages have been collected together. The columns C_{11} , C_{12} and C_{44} show the results of the

Table 15. Elastic constants in $10^{11} \text{ dynes/cm}^2$

Substance	C_{11}	C_{12}	C_{44}	d_{11}	d_{12}	d_{44}	d_{45}
NaCl	4.877	1.232	1.269	4.877	1.34	1.269	1.16
KCl	4.038	0.663	0.628	4.038	0.779	0.628	0.512
KBr	3.455	0.56	0.507	3.455	0.655	0.507	0.412
NaBr	3.87	0.97	0.97	3.87	1.22	0.97	0.72
LiF	11.9	5.38	5.34	11.9	4.5	5.34	6.22
MgO	28.76	8.74	15.14	28.76	11.27	15.14	12.61
AgCl	6.05	3.64	0.624	6.05	3.482	0.624	0.782
Diamond	95	39	43	95	35.9	43.0	46.1
Ge	12.88	4.825	6.705	12.88	4.04	6.705	7.49
Si	16.56	6.386	7.953	16.56	6.56	7.953	7.78
ZnS	10.79	7.22	4.12	10.79	6.17	4.12	5.17
CaF ₂	16.6	4.87	3.58	16.6	4.29	3.58	4.16
Al	10.56	6.39	2.853	10.56	6.29	2.853	2.953
Cu	16.92	12.25	7.55	16.92	12.81	7.55	6.99
Ni	25.26	15.51	12.3	25.26	16.01	12.3	11.8
Ag	12.4	9.34	4.61	12.4	8.89	4.61	5.06

ultrasonic measurements, while the columns d_{11} , d_{12} , d_{44} and d_{45} represents the constants as evaluated from the ultrasonic data in conjunction with the bulk modulus as determined by Bridgman and his collaborators after making *all* necessary corrections. The values of C_{11} and d_{11} are in each case identical; likewise those of C_{44} and d_{44} . But C_{12} and d_{12} are different and such difference is a measure of the failure of the three constant-theory to represent the actual elastic behaviour of the crystal. The difference between d_{44} and d_{45} also expresses the same situation in another way.

Certain general features emerge from the table. For all the four alkali halides which are soluble in water, C_{12} is less than d_{12} and likewise d_{45} is less than d_{44} . This regularity of behaviour taken in conjunction with the reliability of the data in these cases makes it clear that these differences are real and justify us in concluding that the elastic behaviour of cubic crystals cannot be expressed in terms of three constants, but needs four. Diamond, germanium, zinc blende and fluorspar also exhibit a parallel behaviour which is the reverse of that shown by the four water-soluble alkali halides. In their cases, C_{12} is decidedly greater than d_{12} , while *per contra* d_{44} is less than d_{45} and these differences are numerically more striking than in the case of the alkali halides. Magnesium oxide for which the data are reliable exhibits a noteworthy behaviour; the differences between C_{12} and d_{12} and likewise between d_{44} and d_{45} are in the same sense as in the alkali halides but proportionately much larger. Differences of the same order of magnitude but in the opposite sense are shown by lithium fluoride. In the case of the metals crystallising in the face-centred cubic system, we also find differences between C_{12} and d_{12} and between d_{44} and d_{45} , but they are not always in the same sense. This is a feature which need not surprise us in view of the very great differences exhibited by these metals in other respects.

7. Summary

The belief that the elastic behaviour of cubic crystals can be described in terms of three constants rests on theoretical considerations which are examined in the paper and shown to be indefensible. The correct theory demands four constants for cubic crystals belonging to the O_h and T_d classes. The experimental results for sixteen different crystals belonging to these classes for which the most precise data are available are critically examined and it is shown that the adiabatic bulk modulus as computed respectively from the observed velocities of ultrasonic wave propagation and from the static determinations of compressibility made at Harvard are in systematic disagreement. The data show very clearly that the elastic behaviour of these crystals cannot be expressed in terms of three constants, but needs four. The latter have been computed and tabulated.

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The nature of the thermal agitation in crystals

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1. Introduction

The present memoir concerns itself with a problem of fundamental importance in the physics of the solid state, namely the determination of the nature of the atomic movements which constitute the thermal agitation in a crystal. It would be no exaggeration to say that on our taking the correct view of the nature of these movements depends the possibility of our understanding the physical behaviour of crystals aright, not only in the thermal field but also in diverse other fields, as for example their spectroscopic behaviour and the phenomena of X-ray diffraction in crystals. The problem is considered in this paper from two distinct points of view. The first method of approach is to examine the basic experimental facts in the light of fundamental physical principles and to draw the inferences following logically therefrom. The second method of approach is the analytical investigation of the problem on the basis of classical mechanics and the general principles of thermodynamics and the quantum theory. The result in either case is to show that the ideas underlying the well known specific heat theory of Debye and the lattice dynamics of Born and his collaborators are untenable. The picture of the thermal agitation in a crystal which emerges from the present investigation is fundamentally different from that postulated in the theories of Debye and Born.

2. Some general considerations

The identification on a quantitative basis of the thermal energy of a crystal with the energy of atomic oscillations rests on two fundamental ideas; (*a*) that the oscillators can be enumerated, their total number being three times the number of atoms comprised in the crystal; (*b*) that the energy of the oscillators is quantized and for any particular frequency has an average value which can be calculated with the aid of Boltzmann's theorem. We proceed to examine these ideas critically with a view to determine their precise significance as well as their implications.

The first of the two ideas referred to above is based on the fundamental

theorem in classical mechanics which states that all the possible modes of small vibration of a system of connected particles are superpositions of a set of normal modes, the number of such modes being the same as the number of degrees of dynamic freedom of the system, and further that in each such normal mode all the particles of the system have the same frequency of vibration and oscillate in the same or opposite phases. In the present context, therefore, the term oscillator must be considered as referring to a set of atoms vibrating in a normal mode, all of them having the same frequency and the same or opposite phases of vibration.

The second idea, namely that of averaging the energy of an oscillator, arises because of the chaotic nature of thermal agitation which involves energy fluctuations whose magnitude is determined by the frequency of the vibration. The theorem of Boltzmann which enables the average to be calculated is a description in statistical form of the behaviour of the individual units in an assembly consisting of an immense number of such units which are physically identical but differ in their energy states and being in a position to exchange energy with each other form a system in thermodynamic equilibrium. In the present context, the units are the oscillators defined in the preceding paragraph. Hence, if the application of Boltzmann's theorem is to be legitimate, it is necessary to postulate that in the crystal is present an assembly of this nature, viz., a great number of individual oscillators all of which vibrate with the same frequency but are in the different energy states permitted by the quantum theory. For each separate frequency of oscillation, a fresh assembly of that nature is needed to enable the energy for each individual frequency to be separately averaged.

The foregoing theoretical picture of the thermal agitation agrees completely with the actual physical picture in the case under consideration. For, every crystal is itself an assembly of an immense number of similar and similarly situated groups of atoms, the internal vibrations of which can occur with one or another of the characteristic frequencies of the group. The energy of vibration of a group with any one of these frequencies may have any of the series of values allowed by the quantum theory and hence would vary from group to group in an entirely unpredictable manner within the crystal. Such a picture would be in perfect harmony with the basic notions of thermodynamics, but would be wholly irreconcilable with any theory which seeks to identify the energy of thermal agitation with the energy of regular wave propagation in the crystal. But this latter idea is precisely what forms the basis of the specific heat theories of Debye and Max Born. It follows that these theories are fundamentally misconceived and must therefore fail, together with all their consequences.

3. The normal modes of vibration

The normal modes of vibration of the atomic groupings in the crystal referred to above may be determined and enumerated without any difficulty. It is obviously

not permissible in this connection to regard the unit cell in the crystal structure as isolated from the rest of the crystal. For, any oscillation which occurs in a particular cell will necessarily communicate itself immediately to the surrounding cells and set the latter in vibration with the same frequency. Hence, to ascertain the normal modes of vibration, we have to consider vibrations extending over domains whose dimensions are at least as large as the range of the inter-atomic forces. Further, to ensure that the oscillations persist unchanged in character, it is necessary to assume that the oscillation in each of the unit cells included within such a domain is similar and similarly related to the oscillations in the cells surrounding it.

Remembering that in a normal mode the oscillations of all the particles have the same frequency and the same or opposite phase, the foregoing requirements lead us to the following description of the normal modes of vibration: In any normal mode, the oscillations of equivalent atoms in adjoining cells have the same amplitude of vibration but their phases are either the same or the opposite in the cells adjacent to one another along one, two or all three of the axes of the lattice structure. Thus there are $2 \times 2 \times 2$ or 8 possible situations. As a consequence of the identity of the amplitudes of vibration of equivalent atoms in all the cells which need to be considered, the $3p$ equations of motion of the p atoms in any particular cell contain only $3p$ unknowns. Accordingly, it becomes possible to solve the equations completely and determine the $3p$ normal modes and the corresponding frequencies of vibration. As there are eight different situations in respect of the phases of vibration, the equations of motion would necessarily be different in each of them. Accordingly we have $3p \times 8$ or $24p$ normal modes and frequencies of vibration.

An alternative and convenient way of describing the normal modes is to consider a supercell of the lattice whose dimensions are twice as large in each direction as the unit cell. Such a supercell would contain $8p$ atoms and the total number of degrees of freedom associated therewith would be $24p$, and this is the same as the number of normal modes permissible. We may therefore describe these modes as the vibrations of the atoms comprised in the supercell. When this description is adopted, it becomes immediately evident that three of these modes would represent simple translations of the supercell and would therefore have to be excluded in enumerating the internal vibrations of the supercell. We have then left only $(24p - 3)$ normal modes of vibration properly so-called.

4. Wave propagation in crystal lattices

As is well known, the classical theory of elasticity leads to the conclusion that three types of waves can be propagated in any given direction within a crystal with the velocities determined by the density of the material and certain linear

combinations of its elastic constants. The analysis which leads to this result regards the volume elements of the crystal as simple mass particles whose equations of motion can be written down in terms of the tractive forces arising from the elastic strains. Hence the theory and its consequences would cease to be applicable when these assumptions are invalid and the position would then have to be considered afresh from the atomistic standpoint. A formal investigation on the latter basis shows that only in the limiting case of very low frequencies and of correspondingly long waves are the results of the classical theory of elasticity valid. When we enter the region of the higher frequencies, the phase velocity and the group velocity diverge from each other and the very significant result emerges that the group velocity vanishes for $(24p - 3)$ modes of vibration of the lattice. These modes are found to be identical with the $(24p - 3)$ normal modes referred to in the foregoing section.

To avoid breaking the thread of the argument, the detailed dynamical investigation which has been worked out by Dr K S Viswanathan is printed as an appendix to this memoir. It will therefore suffice here to comment on the significance of the results there derived by him. As is very well understood, it is the group velocity which is physically significant in all considerations regarding wave-propagation, since it is a measure of the rate of energy transport in the medium. The vanishing of the group velocity for the whole series of characteristic frequencies of atomic vibration signifies that there is no wave propagation in the real or physical sense of the term when we are considering oscillations in which the interatomic displacements play a significant role. It follows that considerations of the kind used in the classical theory of elasticity to ascertain the normal modes of vibration of a solid body of finite extension are entirely out of place in the atomistic problem. But it is precisely such considerations that are employed in the theories of Debye and Born to describe and enumerate the movements which they identify with the thermal agitation. Thus, even on the basis of the classical mechanics, the ideas underlying those theories are unsustainable and they have therefore to be laid aside as being completely unreal.

5. The frequency spectrum of the thermal agitation

We may sum up what has been said in the foregoing pages by the statement that the energy of the thermal agitation in a crystal may be identified with the energy of an immense number of atomic oscillators which together fill up the volume of the crystal, the individual oscillators being in the various states of excitation corresponding to each of the $(24p - 3)$ frequencies common to them all, supplemented by the energy of the low frequency oscillations which the three omitted degrees of freedom represent. These $(24p - 3)$ frequencies correspond to modes of vibration which are related to the structure of the crystal in precisely

definable terms. It will be seen that this description of the thermal agitation bears no resemblance whatever to that envisaged in the theories of Debye and Born; these authors identify the energy of the thermal agitation with the energy of waves in immense numbers traversing the crystal in all directions and having frequencies which are all different from one another, the energy of the wave of any particular frequency as well as the sum total of the energy of all the waves taken together being distributed uniformly over the volume of the crystal.

It is noteworthy that in his fundamental paper of 1907 introducing the quantum theory of specific heats, Einstein derived his expression for the average energy of an oscillator of given frequency assuming, as is indeed necessary for applying Boltzmann's theorem, that the crystal is an assembly of an immense number of oscillators all having the same frequency but in different energy states and in thermodynamic equilibrium with each other. The theories of Debye and Born make use of Einstein's expression for the average energy of an oscillator, while on the other hand the frequencies of the waves with which they identify the thermal agitation are all different from each other. Thus it will be seen that there is no logical consistency in their approach to the specific heat problem. Further, the uniform distribution of the thermal energy through the whole volume of the crystal which such identification demands is irreconcilable with the fundamental ideas regarding the nature of the thermal energy of material bodies inherent in the Second Law of Thermodynamics, namely, that the distribution of the energy over the volume of the crystal should exhibit fluctuations which are the more violent the higher the frequency of vibration.

The foregoing comments do not by any means traverse all the arguments and assumptions on which the theories of Debye and Born are based. One of the basic objections to their method of approaching the specific heat problem is that since wave motions involve progressive changes of phase along the direction of propagation and may have any frequency assigned to them, they can neither be treated as normal modes nor enumerated. The theories of Debye and Born seek to escape this difficulty by postulating that the number of wave motions is identical with the number of degrees of freedom of the system, while the choice of wavelengths is determined by still another postulate, e.g., the so-called postulate of the cyclic lattice which is claimed to represent the effect of the external boundary of the crystal. Since it is obviously impossible to formulate any boundary conditions for the atomic movements at the external surface of a crystal, the procedure is clearly artificial. But that it is also fallacious becomes evident when we remark that the characteristic modes and frequencies of the atoms in the interior of the crystal are determined exclusively by the structure of the crystal and by the interatomic forces whose range is exceedingly small and hence there exists no justification whatever for the assumption which is inherent in the postulate that these modes and frequencies are influenced by the presence of an external boundary.

6. The spectroscopic behaviour of crystals

It is not proposed in this memoir to discuss how the ideas set forth in it impinge on various aspects of crystal physics. We shall however make a brief reference to those cases in which facts already well established illustrate the validity of the conclusions reached in it.

An Einstein emphasized in his fundamental paper of 1907, the theory of the specific heats of crystals stands in the closest relation to their spectroscopic behaviour. In seeking to explain the data then available for the case of diamond, he made the simplifying assumption that all the oscillators in that crystal have a single common frequency. He recognized however, that in general a crystal would possess several characteristic frequencies and that the expression for its specific heat would involve a summation over them all. In the particular case of diamond, the $(24p - 3)$ frequencies indicated by the present theory are reduced from 45 to 9 in number by reason of the cubic symmetry of the crystal. One of these 9 frequencies represents the triply degenerate oscillation of the two lattices of carbon atoms against each other, while the other eight represent either the longitudinal or the transverse oscillations of the layers of carbon atoms in the cubic and octahedral planes of the crystal. In numerous papers published in these *Proceedings* in recent years, it has been shown that all these nine frequencies can be ascertained by spectroscopic observation and that the specific heat of diamond can be successfully evaluated with the aid of the data thus obtained.

But the case of diamond does not stand alone in this respect. In recent years the spectroscopic behaviour of numerous crystals have been studied by diverse methods, e.g., the scattering of light, absorption in the visible, ultra-violet and infra-red regions of the spectrum, and in particular cases, also their luminescence. The whole of the evidence which has thus come to hand indicates that the vibration spectrum of a crystal consists of a discrete set of monochromatic frequencies and that where there is any departure from this state of affairs, an adequate explanation is forthcoming.

7. X-ray diffraction in crystals

That the atomic vibrations in crystals appear with precisely defined frequencies and with modes bearing a precise geometric relationship to the architecture of the crystal has a most important bearing on the subject of the diffraction of X-rays by crystals. Here again, a particularly striking illustration is furnished by the case of diamond. When a plate of this crystal is traversed by a narrow pencil of X-rays and the resulting Laue pattern is recorded on a photographic plate, it is found that in addition to the usual Laue spots, other sets of sharply defined spots appear on the plate, corresponding to each of the monochromatic components in the

incident X-radiation. This phenomenon which was discovered in the year 1940 by Dr Nilakantan and the present writer using octahedral cleavage plates of diamond has since been thoroughly re-investigated at this Institute by Mr Jayaraman and the writer. The results are found to be in complete accord with the hypothesis that the incident X-radiation excites the triply degenerate oscillation of the two lattices of carbon atoms in the crystal against each other. These movements occur along the directions of the three cubic axes and as a consequence, all the lattice planes of the crystal are disturbed, giving rise to dynamic X-ray reflections by them. *Three* sharply-defined spots corresponding to each monochromatic component in the incident X-ray beam are demanded by the theory for the dynamic reflections by each of the (111) planes of the crystal, since these planes are equally inclined to the cubic axes. These reflections are actually observed in the directions indicated by the theory with suitable settings of the crystal. Other sets of lattice planes in the crystal also give dynamic reflections in the directions demanded by the theory, but since such planes are unequally inclined to the three cubic axes which are the directions of movement of the atoms in the excited oscillations, they are not allequally conspicuous.

Here again the case of diamond does not stand by itself, since analogous phenomena are also exhibited by other crystals. But it is not necessary here to enter into the details of these cases.

8. Summary

The principles of thermodynamics and of the quantum theory indicate that the thermal energy in a crystal is identifiable with the energy of an immense number of atomic oscillators which have their frequencies of vibration in common but are in different states of excitation. Dynamical investigation of the problem shows that if the crystal contains p interpenetrating Bravais lattices of atoms, there are $(24p - 3)$ frequencies of vibration common to all the oscillators. An investigation of the propagation of waves in crystal lattices shows that the results of the classical theory of elasticity are valid only in the limiting case of very low frequencies and proves further that the group velocity of the waves vanishes for $(24p - 3)$ frequencies which may accordingly be identified as the characteristic frequencies of atomic vibration in the crystal. Since there is no wave-propagation in the real or physical sense except in the very lowest range of frequencies, the identification of the thermal energy with the energy of waves traversing the crystal in all directions and having frequencies all different from one another which forms the basis of the specific heat theory of Debye and of Born's lattice dynamics ceases to be justifiable. Other aspects of these latter theories are also examined and it is shown that the assumptions which they involve are untenable and that in consequence the theories have no claim to validity. The experimental results which confirm that the atomic oscillators have specific frequencies in

common and modes of vibration specifically related to the crystal structure are briefly set out.

Appendix

We shall consider the most general case of a crystal whose structure includes p interpenetrating Bravais lattices, all of which are geometrically similar and similarly situated in the crystal arrangement. An unit cell of the crystal will therefore contain p atoms whose masses we shall denote by m_1, m_2, \dots, m_p .

Since a crystal is triply periodic in space, any unit cell can be reached from any other cell of the crystal by the application of three primitive translations or integral multiples of them. We denote the three primitive translations by the three vectors $\mathbf{d}_1, \mathbf{d}_2$ and \mathbf{d}_3 . In the same way, we denote the three primitive vectors of the reciprocal lattice by $\mathbf{b}_1, \mathbf{b}_2$ and \mathbf{b}_3 . In what follows, the symbols s and σ will be used to denote particular cells in the crystal structure while r and ρ will indicate particular atoms in the unit cell; X, Y, Z are three mutually perpendicular directions chosen as the coordinate axes along which the displacements of the atoms from their equilibrium positions are resolved. We represent the displacement-components of any atom, say the r th atom in the s th cell, by means of the symbols $q_{xrs}, q_{yrs}, q_{zrs}$. We can now write the equations of motion of the atoms in the s th cell and they take the form

$$-m_r q_{xrs} = \sum_{y\rho\sigma} k_{xrs}^{y\rho\sigma} q_{y\rho\sigma} \quad \left(\begin{array}{l} x = X, Y, Z \\ r = 1, 2, \dots, p \end{array} \right) \quad (1)$$

The force constant $k_{xrs}^{y\rho\sigma}$ occurring in (1) expresses the proportionality existing between the x -component of the force acting on the atom (r, s) to the displacement in the y -direction of the atom (ρ, σ) which gives rise to this force.

Since the crystal is composed of p different Bravais lattices of atoms, we can reasonably expect a wave of a given wavelength and frequency to be propagated with different amplitudes inside the p different lattices. To solve the set of equations (1), we therefore assume solutions of the form

$$\begin{aligned} q_{xrs} &= A_{xr} \exp [i(\omega t - \mathbf{a} \cdot \mathbf{s})] \\ &= A_{xr} \exp [(2\pi i/\lambda)(vt - \mathbf{e} \cdot \mathbf{s})] \end{aligned} \quad \left(\begin{array}{l} x = X, Y, Z \\ r = 1, 2, \dots, p \end{array} \right) \quad (2)$$

which are plane waves of wavelength λ and circular frequency ω propagating in the direction of the vector \mathbf{e} of the crystal. If we resolve the wave-vector \mathbf{a} along the three axes of the reciprocal lattice and write $\mathbf{a} = \theta_1 \mathbf{b}_1 + \theta_2 \mathbf{b}_2 + \theta_3 \mathbf{b}_3$ then the equations (2) can alternatively be written as

$$q_{xrs} = A_{xr} \exp [i(\omega t - s_1 \theta_1 - s_2 \theta_2 - s_3 \theta_3)] \quad (2')$$

where s_1, s_2 and s_3 are the components of \mathbf{s} along the three Bravais axes of the

crystal. Substituting the equation (2) in (1), we obtain

$$m_r \omega^2 A_{xr} = \sum_{y\rho} A_{y\rho} \left(\sum_{\sigma} k_{y\rho\sigma}^{xrs} \exp(ia \cdot \sigma - s) \right) \quad \left(\begin{array}{l} x = X, Y, Z \\ r = 1, 2, \dots, p \end{array} \right) \quad (3)$$

Equations (3) are a set of $3p$ equations in the $3p$ amplitudes $A_{x1}, A_{y1}, A_{z1}, A_{x2}, \dots, A_{zn}$ of the waves. By eliminating the amplitudes from these homogeneous equations, we can obtain a determinantal equation containing $3p$ rows and $3p$ columns whose elements are the coefficients of the various $A_{y\rho}$'s in the equations (3). By expanding this determinant, we can rewrite this equation in the form

$$s_0 \omega^{6p} + s_1 \omega^{6p-2} + \dots + s_{3p} = 0, \quad (4)$$

in which s_0, s_1, \dots, s_{3p} are functions of the coefficients of the amplitudes in the equation (3), and hence are also functions of the wave-vector of the waves. The roots of the equations (4) are consequently functions of the wavelengths of the waves, in other words, the waves are dispersive. Since an algebraic equation of degree $3p$ has $3p$ roots, for each value of a we obtain $3p$ permissible values for ω which are the roots of (4). Thus there are $3p$ waves of a given wavelength moving in any direction of the crystal.

We shall now consider any one of the $3p$ roots of the equation (4). If this is denoted by ω_k^2 , then ω_k^2 expressed as a function of the wave-vector \mathbf{a} has the following properties:

- (i) ω_k^2 is a periodic function of θ_1, θ_2 and θ_3 with periods 2π for each one of these variables;
- (ii) ω_k^2 is a real function of θ_1, θ_2 and θ_3 ;
- (iii) ω_k^2 is an even function of the wave-vector \mathbf{a} (i.e.), $\omega_k^2(\mathbf{a}) = \omega_k^2(-\mathbf{a})$.

Condition (i) follows from the fact that the coefficients of the amplitudes in (3) are of the form

$$\sum_{\sigma} k_{xrs}^{y\rho\sigma} \exp[i\mathbf{a} \cdot (\sigma - \mathbf{s})] \text{ or } \sum_{\sigma} k_{xrs}^{y\rho\sigma} \exp[i(\sigma_1 - s_1\theta_1 + \sigma_2 - s_2\theta_2 + \sigma_3 - s_3\theta_3)]$$

and hence are periodic functions of θ_1, θ_2 and θ_3 with periods 2π for each of them. The frequencies of the waves which are functions only of these coefficients are therefore also periodic functions of θ_1, θ_2 and θ_3 .

Condition (ii) can easily be understood from physical considerations. Condition (iii) follows from the fact that the frequency of a wave of given wavelength and amplitude should be the same both for waves travelling in one and the opposite directions. Alternatively, these two conditions are consequences of the hermitian property of the coefficients of the amplitudes of the waves in the right-hand side of the equation (3).

Since ω_k^2 is a periodic function of θ_1 , θ_2 and θ_3 we can express it as a three-dimensional Fourier-series in the form

$$\omega_k^2 = \sum_{n_1, n_2, n_3} \sum_{-\infty}^{+\infty} A_{n_1 n_2 n_3} \exp [i(n_1 \theta_1 + n_2 \theta_2 + n_3 \theta_3)] \quad (5)$$

where the summation extends over all integral values of n_1 , n_2 and n_3 from $-\infty$ to $+\infty$.

If we use a single symbol \mathbf{n} to denote the triplet $(n_1 n_2 n_3)$ we can rewrite (5) also in the form

$$\omega_k^2 = \sum_{\mathbf{n}} A_{\mathbf{n}} \exp(i\mathbf{a} \cdot \mathbf{n}) \quad (6)$$

Since ω_k^2 is real, the coefficients of $\exp i(n_1 \theta_1 + n_2 \theta_2 + n_3 \theta_3)$ and $\exp -i(n_1 \theta_1 + n_2 \theta_2 + n_3 \theta_3)$ in (5) should be complex conjugates. Hence we have

$$A_{\mathbf{n}} = \bar{A}_{-\mathbf{n}} \quad (7)$$

Now by writing $-\mathbf{a}$ for \mathbf{a} in (6), we get

$$\omega_k^2(-\mathbf{a}) = \sum_{\mathbf{n}} A_{\mathbf{n}} \exp(-i\mathbf{a} \cdot \mathbf{n}) \quad (8)$$

Since from condition (iii), $\omega_k^2(-\mathbf{a}) = \omega_k^2(\mathbf{a})$ we see by a comparison of (6) and (8) that

$$A_{\mathbf{n}} = A_{-\mathbf{n}} \quad (9)$$

Combining (7) and (9) we get

$$A_{\mathbf{n}} = \bar{A}_{-\mathbf{n}} = \bar{A}_{\mathbf{n}} \quad (10)$$

or $A_{\mathbf{n}}$ is real.

We can therefore rewrite (5) as

$$\begin{aligned} \omega_k^2 &= A_{000} + 2 \sum A_{n_1 n_2 n_3} \cos(n_1 \theta_1 + n_2 \theta_2 + n_3 \theta_3) \\ &= A_{000} + 2 \sum_{\mathbf{n}} A_{\mathbf{n}} \cos \mathbf{a} \cdot \mathbf{n}, \end{aligned} \quad (11)$$

where the summation now is over all lattice points on and above any one of the lattice planes $\mathbf{d}_1 = 0$ or $\mathbf{d}_2 = 0$ or $\mathbf{d}_3 = 0$.

We shall assume that the series obtained by differentiating term by term the sum on the right-hand side of (11) converges uniformly for all values of θ_1 , θ_2 and θ_3 in the interval $(0, 2\pi)$. Then, we have

$$2\omega k \frac{d\omega_k}{da} = -2 \sum A_{\mathbf{n}} \mathbf{e} \cdot \mathbf{n} \sin \mathbf{a} \cdot \mathbf{n}. \quad (12)$$

Now, when θ_1 , θ_2 and θ_3 each takes one of the values 0 or π , $\sin \mathbf{a} \cdot \mathbf{n}$ (i.e.)

$\sin(n_1\theta_1 + n_2\theta_2 + n_3\theta_3)$ is equal to zero. Hence if

$$\omega_k \neq 0 \quad (13)$$

for these values of θ_1 , θ_2 and θ_3 , we find from (12) that

$$\frac{d\omega_k}{da} = 0$$

whenever

$$\begin{aligned} \theta_1 &= 0 \text{ or } \pi; \\ \theta_2 &= 0 \text{ or } \pi; \\ \theta_3 &= 0 \text{ or } \pi. \end{aligned} \quad (14)$$

When $\theta_1 = 0$; $\theta_2 = 0$; $\theta_3 = 0$, it can be proved that three of the roots of (4) will become zero and hence the condition (13) is not satisfied. These are the limiting cases of elastic vibrations of long wavelength in the crystal and for them, since $\omega_k \rightarrow 0$ as $a \rightarrow 0$

$$\lim_{a \rightarrow 0} \frac{\omega_k}{a} = \frac{d\omega_k}{da} \quad (k = 1, 2, 3),$$

and therefore the group and wave velocities became identical with the velocities of propagation of the elastic vibrations in the crystal lattice.

The eight set of cases considered above now yield a total number of $24p$ frequencies. Leaving out of these the three degrees of freedom pertaining to pure translations and for which, as we have seen, the group velocity is non-zero being equal to its wave velocity, we get $(24p - 3)$ frequencies for which the group velocity of the waves vanishes. The modes associated with these frequencies now possess a simple geometric description. By substituting the values of 0 or π for θ_1 , θ_2 and θ_3 in (2'), it can easily be seen that in all the $(24p - 3)$ cases referred to above, equivalent atoms in adjacent cells vibrate with the same amplitude and with the same or opposite phases along one, two or all three of the Bravais axes of the crystal. Since the group velocity is zero, any disturbance with these frequencies remains centred in the region of its origin. Further, the phase relationships for these $(24p - 3)$ modes are exactly the same as those demanded for the normal vibrations of a connected system of particles.

The thermal energy of crystals*

SIR C V RAMAN

The determination of the nature of the atomic movements which constitute the thermal agitation in a crystal is a fundamental problem in the physics of the solid state. Its importance will be evident when it is remarked that even the most familiar aspects of the thermal behaviour of solids depend for their explanation on the precise nature of these movements. The subject also stands in the closest relationship with the spectroscopic behaviour of crystals and with X-ray crystallography, to say nothing of various other branches of physics.

Since the atomic movements under consideration are of thermal origin and are presumably in the nature of vibrations about the atomic positions of equilibrium, the subject has to be viewed in the light of the fundamental principles of thermodynamics and the quantum theory. However, as in the parallel problem of the vibration spectra of molecules, we have to seek the aid of classical mechanics for ascertaining the modes and frequencies of vibration with which we are concerned.

2. Thermodynamic considerations

Every crystal is a three-dimensional grouping in space of atoms held together by their mutual interactions; equivalent atoms in the crystal are located at the points of a Bravais lattice, and if the crystal consists of p interpenetrating Bravais lattices, there would be p atoms in each unit cell of the crystal structure. Since the frequencies of vibration of the atoms are determined by their masses and by the interatomic forces which are of limited range, they would necessarily be the same for the group of atoms contained in every cell of the structure. Hence every crystal may be considered as an assembly of a great number of oscillators physically similar to each other and having a set of vibration frequencies in common, and which since the oscillators can exchange energy with each other, constitute a system in thermodynamic equilibrium. Each oscillator can for any particular frequency of vibration assume any of the energy states permitted by the quantum

*“The nature of the thermal agitation in crystals,” by Sir C V Raman, Memoir No. 77 from the Raman Research Institute, Bangalore, and *Proc. Indian Acad. Sci.* **42** 163–74 (1955).

theory, the probability of its being present in any one state being given by Boltzmann's well known formula. The energy of the entire assembly of oscillators can therefore be evaluated by multiplying the number of oscillators of any particular frequency by the average energy of an oscillator of that frequency which is calculable from the relative probabilities of its different energy states, and then summing up the results for all the frequencies. The total number of oscillators included in such a reckoning would be three times the number of atoms comprising the crystal. This follows from the theorem in classical mechanics which states that the number of normal modes of vibration of a connected system of particles is the same as the number of degrees of freedom of movement of the entire system.

3. Dynamical theory

The dynamics of atomic vibration in a crystal may be dealt with from two different standpoints which may be designated as the "molecular" and "molar" points of view respectively. In the "molecular" approach to the problem, we fix our attention on a particular unit cell of the crystal structure and proceed to write down and solve the $3p$ equations of motion of the p atoms contained in it, with a view to discover and enumerate their normal modes of vibration. In doing this we have necessarily to take account of the forces arising from the movements of the atoms in the surrounding cells which interact with those in the cell under consideration. It is obvious that no mode of vibration of the atoms in the unit cell can persist unchanged unless the atoms in the surrounding cells also vibrate in a similar mode with the same frequency. This would be the case if equivalent atoms in these outer cells also vibrate with the same amplitudes, but as regards their phases of vibration, there are several distinct possibilities. A formal investigation shows that there are $2 \times 2 \times 2$ or eight possibilities in all which can be described as follows: The phases of equivalent atoms are either the same or else opposite in consecutive cells along one, or two, or all the three axes of the Bravais lattice. The identity of the amplitude of vibration of equivalent atoms reduces the number of independent co-ordinates to $3p$ only. Thus, the equations can be solved and result in $3p$ solutions, but as there are eight different situations in respect of the phases, we have $8 \times 3p = 24p$ solutions in all. This is the same as the number of degrees of dynamic freedom of the $8p$ atoms contained in a super-cell having twice the linear dimensions of the unit cell of the crystal structure. Accordingly, we recognize $(24p - 3)$ normal modes of vibration properly so-called, the three omitted degrees of freedom representing the translatory movements of the super-cell.

In the "molar" approach to the problem, we consider the entire crystal as a single physical entity and investigate the propagation of waves through its structure. The wave equations are found to be formally satisfied if it be assumed that the equivalent atoms located at the points of a Bravais lattice have the same

amplitude of vibration, this however being different for the different lattices of atoms, while the frequency, wavelength and the direction of the wave-vector are the same for all the interpenetrating lattices. Proceeding to solve the set of $3p$ equations obtained on this basis, an algebraic equation of degree $3p$ for the frequency results, and the solution of this gives us $3p$ different frequencies for a wave of given wavelength travelling in any assigned direction. By considering the functional dependence of these $3p$ frequencies on the wavelength and direction of propagation, it is found that the group-velocity of the waves vanishes for $(24p - 3)$ frequencies associated with eight different wave-vectors in the crystal. The $(24p - 3)$ frequencies thus obtained and the corresponding modes of vibration are found to be the same as the frequencies and normal modes deduced by the "molecular" approach to the problem, namely, those in which equivalent atoms in consecutive cells vibrate with the same amplitude and with phases that are either the same or else opposite along one, two or all three of the Bravais axes of the crystal. They may therefore be identified as the characteristic or normal modes and frequencies of vibration of the crystal structure. The three omitted frequencies represent the limiting case of the three sets of waves of the lowest frequencies and the longest wavelengths for which the group velocity does not vanish but comes out as equal to the phase-velocity of the waves. These cases are identifiable with the three types of waves whose propagation in any direction in the crystal is shown to be possible by the classical theory of elasticity. The vanishing of the group velocity for all the $(24p - 3)$ frequencies characteristic of the lattice structure is significant. It indicates that no wave-propagation in any real or physical sense is possible in a crystal except in the lowest range of frequencies where alone the ideas and results of the classical theory of elasticity possess any validity.

4. The spectrum of the thermal agitation

The results of the dynamical theory enable us to complete the thermodynamic picture already indicated above in outline. The p interpenetrating Bravais lattices of atoms constituting the crystal represent an assembly of atomic oscillators which have a set of $(24p - 3)$ vibration frequencies in common. Each of these oscillators can assume one or another of the various energy states for these frequencies permitted by the quantum theory, the relative probabilities of the same being given by the Boltzmann formula. It would not be possible to specify or predict which of the great number of oscillators in the crystal would be in a particular excited state for any of its possible frequencies of vibration at any given instant. In other words, the thermal energy would be distributed through the volume of the crystal in a manner which fluctuates from place to place and from instant to instant in an unpredictable fashion. The fluctuating character of the energy distribution would be the more striking, the higher the frequency under

consideration, since the energy jumps indicated by the quantum theory are proportional to the frequency.

Thus, it emerges that $(24p - 3)$ out of every $24p$ degrees of freedom of atomic movement in the crystal manifest themselves in the thermal agitation as modes of internal vibration with a precisely defined set of monochromatic frequencies and in modes specifically related to the crystal structure, though they are localised in the crystal in a chaotic and unpredictable fashion. The residual 3 degrees out of every $24p$ degrees of freedom represent, as we have seen, the translatory movements of the super-cells of the crystal lattice. Such movements would disturb the regularity of the crystal structure, in other words, would give rise to stresses and strains of the same general nature as those contemplated in the classical theory of elasticity. Hence, the 3 residual degrees of freedom would also manifest themselves in the thermal agitation as oscillations localised in the crystal in a chaotic and unpredictable fashion, but since the moving masses are now larger, the frequencies would necessarily be lower, being determined by the dimensions of the volume elements which can be regarded as the individual oscillators: the larger these volume elements are, the fewer of them would be needed to fill the crystal and the lower also would be the frequency. Thus, the spectrum of the thermal agitation resulting from movements of the kind under consideration would stretch over a range of frequencies down to low values, but the upper parts of the range would be much more densely populated than the lower.

5. Remarks on some earlier theories

The attentive reader would have noticed that the picture of the thermal agitation in a crystal and its spectroscopic characters which has emerged bears no resemblance whatever to that figuring in the well known theory of the specific heat of crystals put forward by Debye and in the lattice theory of Max Born and his collaborators. These authors identify the energy of the thermal agitation in a crystal with the energy of an immense number of waves traversing the crystal in all possible directions and of which the frequencies are all different. But nevertheless in evaluating the total energy, these authors make use of the expression for the average energy of an oscillator derived by Einstein for an assembly consisting of an immense number of oscillators having an identical frequency of vibration. In the circumstances, it would not be superfluous to set out briefly the considerations which show that the theories of Debye and Born are fundamentally misconceived and that the conclusions to which they lead are completely unreal.

I. The theory of the specific heat of crystals has necessarily to be based on the theorem in classical mechanics which states that the normal modes of vibration of a connected system of particles form an enumerable set equal in number to the

number of degrees of dynamical freedom of the system and that in each such normal mode, all the particles vibrate with the same or opposite phases. Waves are not normal modes, since the phase alters progressively in the direction of the wave-vector, and hence it is an obviously fallacious procedure to seek to found a theory of specific heat on the basis of wave-motions.

II. A dynamical investigation shows that waves of the kind contemplated by the classical theory of elasticity in which the phase-velocity is equal to the group velocity are only possible in the limiting case of very low frequencies and of very great wavelengths. It also shows that the atoms in a crystal form an assembly of oscillators which have a set of $(24p - 3)$ vibration frequencies common to all, and hence form a system to which the principle of Boltzmann can be legitimately applied to determine the average energy of an oscillator of each frequency and thereby to evaluate the total energy of the system.

III. The fundamental principles of thermodynamics and the quantum theory indicate that the thermal agitation in a medium consisting of material particles capable of vibrating about their positions of equilibrium is of a chaotic and unpredictable character, exhibiting fluctuations in the energy of the vibration from place to place and from instant to instant whose magnitude is determined by the frequency of vibration and hence would be different for each different frequency. It would be patently absurd to identify such a disturbance in the crystal with waves of constant amplitude spread over its volume.

IV. The identification of the thermal energy of a crystal with the energy of waves traversing it in all directions and having frequencies all different from each other leads to a totally false picture of the spectroscopic behaviour of crystals, as is shown by several independent methods of experimental investigation. For instance, all crystals usually exhibit at room temperature and always when cooled down to low temperatures the sharply defined shifts of frequency in the spectrum of monochromatic light scattered by them, corresponding to each of the $(3p - 3)$ frequencies of the structure active in light-scattering. Significantly also, overtones and combinations of these $(3p - 3)$ frequencies and of the remaining $21p$ frequencies manifest themselves with observable intensity as sharply defined frequency shifts with many crystals.

V. That the identification of the thermal agitation in a crystal with waves traversing the solid is a misconceived idea is also apparent from the complete dissimilarity between heat energy and sound energy in their observable behaviour. The latter travels through a crystal with a velocity of some thousands of metres per second, while heat energy merely diffuses through it.

Quantum theory and crystal physics*

SIR C V RAMAN

1. Introduction

The physics of the twentieth century differs fundamentally from the physics of the nineteenth mainly because of two theories known respectively as the Quantum Theory and the Theory of Relativity which form an integral part of its scheme of thought. It is these two theories that have enabled a far deeper understanding of the nature of the physical world to be attained than was possible at the end of the last century. One must here acknowledge the work of Albert Einstein who played the leading role in the development of both of these theories. His publications during the first two decades of the present century bear on every page the imprint of a powerful and penetrating intellect. Even after this lapse of years, the physicist of today will find the study of those papers a profitable and stimulating experience. Indeed, a good deal of what I have to say in this address only reflects the results of such a study in relation to the fundamental problems of the crystalline state of matter—a subject which has deeply interested me for several years past.

2. Origin of the quantum theory

The quantum theory arose from the attempt to explain the characters of the radiation which emerges from the window of an enclosed furnace heated to high temperatures. As is well known, the total intensity of such radiation increases rapidly with rise of temperature of the furnace. Simultaneously, there is a shift of the spectral maximum of intensity towards higher frequencies, as is indeed evident from the progressive change in colour of the radiation. Thermodynamic considerations indicate that this shift should occur in such a manner that the spectral frequency at the point of maximum intensity should be directly proportional to the absolute temperature of the furnace. Quantitative measurements confirm that this is the case and show that the changes in the intensity as well as in the spectral character of the radiation with rise of temperature agree

* Presidential address to the Indian Academy of Sciences, at Waltair, on the 26th December 1956.

with a formula for the spectral intensity in which the cube of the spectral frequency appears multiplied by an exponential function of a type made familiar by Boltzmann's well known principle. The argument of the exponential function is negative and has as its numerator the spectral frequency multiplied by one universal constant and as its denominator the absolute temperature multiplied by another universal constant. A small but important modification secures a much more satisfactory agreement between the formula and the facts of observation. In the modified expression, the exponential has the same argument with a positive sign and now appears in the denominator with unity subtracted from it. This is the celebrated Planck formula except for a multiplying numerical factor.

3. Einstein's derivation of the Planck formula

Einstein gave a physical interpretation of the Planck formula and also showed how the formula could be derived on the basis of simple physical considerations. He interpreted the formula to mean that radiation of all frequencies is emitted and absorbed by material bodies in discrete quanta of energy proportional to their respective frequencies. He also showed that the radiation formula follows very naturally if we assume that the energy of the material particle which emits the radiation is itself quantised, in other words, its energy of vibration alters by successive steps, each of which is equal to the quantum of radiation energy which is emitted in the process.

A more complete and logically satisfying derivation of the Planck radiation formula was given by Einstein ten years later, viz., in 1917. In that paper, the notion of probability which in the quantum theory replaces the determination of the older physics finds a prominent place. Instead of assuming the radiator to be a harmonic oscillator as in his paper of 1907, Einstein dealt with the most general case of an oscillator which has a number of discrete energy levels. The probability of its being present in any one of them is expressed by the product of the inherent statistical weight characteristic of the level multiplied by the appropriate thermodynamic probability factor. The latter takes the form of an exponential function with a negative argument equal to the energy of the state divided by the product of the absolute temperature and the Boltzmann constant. Einstein then considers the probability of three different kinds of elementary processes occurring in any given small time interval. The first is a spontaneous transition from the higher to a lower state of energy with emission of radiation as contemplated in Bohr's theory of spectra; the second is a transition of the same nature but now induced by the presence of an external radiation field; the third is a transition from the lower to the higher energy state also induced by the external field. The probabilities of the two latter transitions are taken as proportional to the energy density in the surrounding radiation field. A transfer of energy from

the oscillator to the field and an absorption of energy from the field by the oscillator are involved respectively in the two processes. In a steady state of affairs, the probabilities of transition in the two opposite directions must necessarily balance each other. These considerations lead at once to the Planck radiation formula.

4. The crystal as an assembly of oscillators

The foregoing exposition of Einstein's original ideas is intended to furnish a theoretical background for a consideration of the fundamental properties of the solid state which is the subject of the present address. Elementary processes closely analogous to those contemplated in Einstein's paper of 1917 successfully describe the phenomena actually observed when a beam of monochromatic light traverses a crystal and the light diffused in its interior is examined spectroscopically. We observe in the spectrum of the scattered light sharply defined lines with frequencies both higher and lower than that of the incident radiation. The ratio of the intensities of each such pair of lines having equal spectral displacements in opposite directions is found to be expressed correctly by a Boltzmann factor corresponding to the change of frequency multiplied by Planck's constant, this again being multiplied by the fourth power of the ratio of the two spectral frequencies. These facts indicate that the displaced frequencies arise from transitions from a higher to a lower energy state and vice versa induced in the elementary oscillators comprised in the crystal by the incident radiation. We are thus naturally led to regard the crystal as an assembly of a great number of oscillators which form a system in thermodynamic equilibrium. The thermal energy of the crystal may then be equated to the sum of the thermal energies of all the oscillators of the different sorts of which it is composed.

It is evident from what has just been stated that the specific heats of crystals stand in the closest relation to their spectroscopic properties. The first step in the theoretical evaluation of the thermal energy of the crystal is accordingly to identify and enumerate the oscillators of which it is composed and to discover and specify the energy states which they can occupy.

5. The oscillators and their energy levels

To begin with, we may provisionally identify the oscillators with whose behaviour we are concerned with the groups of atoms present in the unit cells of the crystal structure. To discover the energy levels which these oscillators can occupy, we may, at least in regard to the infra-red or vibrational levels, adopt the same procedure as that which has proved itself abundantly successful in the field of molecular spectroscopy. As is well known, that procedure consists in

determining and enumerating the different possible modes of vibration in each one of which the atoms all vibrate with the same frequency and in the same or opposite phases.

In endeavouring to carry through the procedure indicated above, the difficulty immediately presents itself that the group of atoms present in any one unit cell of the crystal structure is not isolated but forms a connected system with the groups of atoms in the surrounding cells and these latter again are connected with groups of atoms further out and so forth. The mathematical and physical difficulties which present themselves by virtue of these inter-connections disappear when we make use of the fundamental property of crystal structure, viz., that it comes into coincidence with itself following a unit translation along any one of its three axes. Hence any normal mode of vibration should also possess the same property viz., it remains a normal mode following a unit translation of the crystal. This requirement immediately enables us to determine and enumerate the normal modes in the most general case of a crystal consisting of several interpenetrating Bravais lattices of equivalent atoms. It emerges that the normal modes are divisible into two classes; in the first class, the amplitudes as well as the phases of oscillation of equivalent atoms in adjoining cells of the lattice structure are identical, while in the second class of normal modes the amplitudes of equivalent atoms are the same but the phases are reversed along one or two or all three of the axes of the lattice. If the crystal consists of p interpenetrating Bravais lattices, there are $(3p - 3)$ normal modes of the first class and $21p$ modes of the second class.

Thus the result emerges that the vibrational energy levels of a crystal form a sharply defined set in much the same manner as the vibrational energy levels in the spectra of molecules. But this result would necessarily be modified when the effects of anharmonicity and the interactions of the different normal modes with each other are taken into consideration.

6. The spectroscopic behaviour of crystals

The theoretical results stated above are in complete agreement with the actual spectroscopic behaviour of crystals in the infra-red region of frequencies as revealed by diverse techniques of observation in appropriate physical conditions. For example, they furnish an immediate explanation of the spectroscopic effects exhibited by crystals in the scattering of monochromatic light as mentioned earlier. In some cases the energy levels are shown by the spectral shifts to exhibit a lack of sharpness. That this arises from the disturbing effects of anharmonicity is demonstrated by cooling down the crystal to liquid-air temperature. The energy levels then become perfectly sharp, as is to be expected. We need not dilate here upon the different techniques of spectroscopic observation which are available only in particular cases. Mention should be made, however, of the very general

method of observing the energy levels in crystals by the techniques of infra-red absorption. These latter have been greatly improved of recent years and the results obtained with such improved techniques completely confirm the theoretical findings stated above.

A feature of special interest to which reference may be made here is in respect of the possibility of observing the $21p$ normal modes of the second class in which the phases of oscillation are opposed in adjoining cells of the crystal structure. It is to be expected that by reason of such opposition of phase these modes would be precluded from observation by any of the available methods of spectroscopic study. Fortunately, however, and for reasons which I shall not here dilate upon, this is not invariably so. The normal modes of the second class are actually accessible to observation in several cases and they then manifest themselves as discrete and sharply defined lines in the spectra, provided the effects of anharmonicity are either absent or else are suppressed by the use of adequately low temperatures. Their appearance is one of the most striking vindications of the correctness of the present theoretical approach.

7. The specific heats of crystals

Regarding a crystal as an assembly of an immense number of oscillators in thermodynamic equilibrium, the evaluation of its thermal energy as a function of the temperature reduces itself to the problem of classifying and enumerating the different sorts of oscillators comprised in it and determining the scheme of energy levels for the oscillators of each sort. An application of Boltzmann's principle then enables us to evaluate the average energy of an oscillator of that sort, and multiplying it by the number of such oscillators we obtain a sum total; the addition of the sums thus found for the different sets of oscillators gives the total thermal energy of the crystal. By differentiating this total with respect to the temperature, we obtain the specific heat of the crystal.

As already stated, we have $(3p - 3)$ normal modes of vibration of the first kind and $21p$ normal modes of the second kind. Thus, we have $(24p - 3)$ modes and frequencies in all and these have equal statistical weight. They may be regarded as the internal modes of vibration of the $8p$ atoms contained in a volume element of the crystal whose dimensions are twice as large in each direction as the unit cell of the crystal structure. The three omitted degrees of freedom represent the translatory movements of these groups of $8p$ atoms each. If we leave the latter aside for a moment and also neglect the effects of anharmonicity, the specific heat of a crystal may be expressed very simply as the sum of $(24p - 3)$ Einstein functions, each involving its own characteristic frequency; the total number of oscillators which contribute is the number of groups of $8p$ atoms each comprised in the crystal. To this sum must be added the contribution to the specific heat arising from the oscillations inside the crystal which are attributable to the translatory

movements of these groups of $8p$ atoms each. In a paper which has appeared in the October issue of the *Proceedings* of the Academy, it has been shown how the latter contribution may be rigorously evaluated. The argument by which this is affected may be very simply stated. The translatory movements of the groups of $8p$ atoms each give rise to oscillatory movements in volume elements which comprise a still larger number of atoms. By taking a succession of volume elements of different sizes and taking note of the circumstance that the lower limit of frequencies of vibration thus arising would diminish in proportion to the increasing dimensions of the volume element, the spectral distribution of frequencies follows immediately. Their contribution to the thermal energy of the crystal is found to be expressible as an integral having a well known form involving Einstein's expression for the average thermal energy of a harmonic oscillator.

It may be mentioned in conclusion that the method sketched above has been successfully applied to the evaluation of the specific heats of crystals—including especially diamond and the metallic elements—down to the very lowest temperatures approaching absolute zero. The theory emerges triumphantly from the test.

8. Summary

The fundamental notions of quantum theory and thermodynamics indicate that a crystal should be regarded as an assembly of an immense number of oscillators whose energy states are quantised and which form a system in thermodynamic equilibrium. They also indicate that the spectroscopic properties and the thermal behaviour of crystals stand in the closest relation to each other. We are thus left with the problem of discovering and enumerating the oscillators of the different sorts comprised in the crystal and of determining their scheme of energy levels. This may be done by methods analogous to those which have proved successful in the field of molecular spectroscopy. The results obtained are in perfect agreement with the observed spectroscopic properties and thermal behaviour of crystals.

The physics of crystals*

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1. Introduction

It is the aim of this address to give a fresh orientation to the subject of crystal physics. We begin with a re-examination of the fundamental notions on which a theoretical approach to the problems of the subject has to be based. The ideas which emerge are then applied to find an answer to the following questions: What is the nature of the thermal agitation in crystals? What is the character of their vibration spectra? These questions are of fundamental importance since they confront us in any attempt to explain or interpret the physical behaviour of crystals. The results which emerge from our enquiry impinge on many aspects of crystal physics. But we shall restrict ourselves here to a consideration of those in which the relationships between theoretical reasoning and factual experience are most evident, viz., the thermal properties of crystals and their spectroscopic behaviour. Even in these fields, we can here do no more than broadly indicate the general nature of the results which follow from the application of the new ideas.

2. The theory of Einstein

It is appropriate that we begin with a reference to the classic paper of 1907 by Einstein introducing the quantum theory of specific heats, a paper which even fifty years after its publication remains worthy of careful study. Einstein commences his paper by showing that the acceptance of Planck's radiation formula demands as a necessary consequence that the energy of a resonator capable of absorbing or emitting radiation with a specific frequency can only increase or diminish by quanta proportional to that frequency. *It is inferred that*

* Address to a Conference of Nobel Laureates at Lindau on the Lake of Constance, June 25th to 29th, 1956.

the energy of any elementary structure capable of mechanical vibration should likewise obey the quantum rule. Einstein then indicates a procedure which enables this principle to be applied to the case of crystals. He identifies the thermal energy of a crystal with the mechanical energy of vibration of an immense number of *individual* oscillators distributed over its volume, the total number of these oscillators being the same as thrice the number of atoms comprised in the crystal. It is assumed that the oscillators could be grouped into sets; each set comprises a great number of individual oscillators characterised by a common frequency of vibration. The individual oscillators in each set occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The numbers occupying these levels are in the relative proportions determined by the respective energies and by the temperature as indicated by the principle of Boltzmann. The average energy of an oscillator in each of the sets is then evaluated. Summing up over all the oscillators in each of the sets, and then over all the sets, Einstein obtains an explicit formula for the thermal energy of the crystal as a function of the temperature.

Examining the procedure thus summarised, it is evident that every step in the argument can be justified. A crystal is an assembly of a great number of similar and similarly situated groups of atoms, the normal modes and frequencies of vibration of which would necessarily all be identical. The total number of degrees of dynamical freedom of the entire system may accordingly be divided up into sets, each set representing a great number of individual oscillators having a common frequency. Since these oscillators are interconnected, they can exchange energy with each other and thereby constitute a system in thermodynamic equilibrium of which the behaviour could be statistically described in terms of Boltzmann's principle. In other words, the procedure followed effects a synthesis of the results of classical dynamics with the notions of the quantum theory and the basic principles of thermodynamics. The simplicity of Einstein's theory is as noteworthy as its success in explaining the general character of the specific heat-temperature curve of crystals.

We conclude, therefore, that Einstein's approach to the problem is fundamentally correct. His theory indicates that the atomic vibration spectrum of a crystal would consist of a set of discrete monochromatic frequencies, their number being the same as the number of sets of oscillators which are the carriers of the thermal energy. By virtue of Boltzmann's principle, the distribution of this energy over the volume of the crystal would exhibit fluctuations both in space and in time, the magnitude of the fluctuations being the greater the higher the frequency of the oscillators under consideration. However, the theory as it stands gives no precise indication of how the oscillators in each set are to be enumerated and how their respective frequencies of vibration are to be determined. Neither is any indication given whether the modes of vibration of the solid recognised by the classical theory of elasticity have any place in the picture. We shall now proceed to show how these lacunae in Einstein's theory may be filled up.

3. The dynamics of crystal lattices

The fundamental role which the enumeration of the degrees of freedom of atomic movement plays in specific-heat theory derives its justification from the well-known theorem in classical mechanics regarding the small vibrations of a connected system of particles about their positions of equilibrium. This theorem states that all the possible oscillations of the system are superpositions of its normal modes of vibration in each of which all the particles of the system vibrate with the same frequency and in the same or opposite phases. On the other hand, in Einstein's theory we are concerned with the modes and frequencies of vibration of the *individual* oscillators of which the total number is equal to the number of degrees of dynamical freedom of the entire system. These two points of view can be reconciled by identifying the normal modes and frequencies of vibration which are characteristic of the structure of the crystal with those that describe the dynamical behaviour of the elementary units of which it is composed.

The fundamental property of crystal structure is that it comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Hence, the normal modes of vibration characteristic of the structure of a crystal should satisfy a similar requirement. This can evidently happen in two ways, viz., the amplitudes and phases of oscillation of equivalent atoms in adjacent cells are the same; alternatively, the amplitudes are the same while the phases are all reversed following the unit translation. Since these two possibilities exist for each of the three axes of the lattice, we have $2 \times 2 \times 2$ or eight possible situations. In each of these situations, the equations of motion of the p atoms contained in the unit cell can be completely solved, yielding us $3p$ solutions. Thus in all, we have $24p$ solutions from which the three simple translations must be excluded. We are then left with $(24p - 3)$ normal modes and frequencies of vibration. Thus, the fundamental result emerges that a crystal consisting of p interpenetrating Bravais lattices of atoms has $(24p - 3)$ characteristic modes of vibration, each of which is characterised by a specific frequency. In $(3p - 3)$ of these modes, equivalent atoms have the same amplitudes and phases of oscillation in the adjacent cells, while in the $21p$ other modes the amplitudes are the same, while the phases alternate in adjacent cells along one, two or all three of the axes of the lattice.

The $(24p - 3)$ normal modes of vibration indicated by the preceding argument may obviously be regarded as the modes of internal vibration of the group of $8p$ atoms comprised in a supercell of the crystal lattice whose linear dimensions are twice as large as that of the unit cell containing p atoms. The 3 omitted degrees of freedom would then represent the 3 degrees of translatory freedom of movement of the whole group of $8p$ atoms included in the supercell. Thus, it emerges that the structural unit whose dynamical behaviour is representative of the entire crystal is not the unit cell of the crystal structure but is twice as large in each direction as the latter.

4. The vibration spectrum of a crystal

The considerations set forth above indicate that a crystal may be regarded as an assembly consisting of $(24p - 3)$ sets of similar oscillators, each with its own distinctive vibrational frequency. Even a monoatomic crystal for which $p = 1$ would have 21 characteristic frequencies, while a diatomic crystal for which $p = 2$ would have 45 and so forth. The number of distinct frequencies would however be reduced considerably if the crystal belongs to a class with a high degree of symmetry. For instance, it can be readily shown that a face-centred cubic lattice of atoms would have only four characteristic frequencies of vibration, while cubic crystals such as diamond and rock-salt having two non-equivalent atoms in the unit cell would each have nine distinctive frequencies. The important point to be emphasised is that the vibration spectrum of a crystal consists of a set of discrete monochromatic frequencies whose number is the greater, the more numerous the atoms included in its unit cell are or the lower the symmetry of the crystal.

To complete the picture, we have to consider the nature of the movements associated with the three omitted degrees of freedom representing the translatory movements of the supercell of the crystal lattice. Such translations would necessarily result in local stresses and strains of the same general nature as those contemplated in the theory of elasticity and hence would also give rise to localised oscillatory movements. In other words, to complete the picture of the thermal agitation envisaged in Einstein's theory, we have to superpose on the oscillations of precisely defined frequencies determined by the atomic structure of the crystal, other quantized oscillations whose frequencies are not so precisely defined, since they would depend upon the dimensions of the moving masses and the forces thereby brought into play. It is evident that the smaller the mass of the oscillators under consideration, the more numerous they would be and also the higher their frequencies of vibration. It follows that the spectrum of the thermal agitation represented by such movements would be continuous and would exhibit a concentration of frequencies most marked at the upper end of the frequency range and falling off rapidly to zero as we move towards the lower end of the range.

5. The theories of Debye and Born

The views set forth above regarding the nature of the thermal agitation in crystals and the character of their atomic vibration spectra are essentially a justification and a development of the original ideas of Einstein outlined in his fundamental paper of 1907. It is a matter of scientific history, however, that an approach of an entirely different nature to the problems of crystal physics was put forward a few years later and found general acceptance. The reference here is to Debye's theory of specific heats familiar to all students of physics and chemistry and to the lattice

dynamics of Born and his collaborators which is regarded with favour by the mathematical theorists. The theories of Debye and Born differ in detail, but the basic idea in both is the same, namely that we are here dealing with a boundary value problem in the theory of wave-propagation. Actually, what we are concerned with is the determination of the modes and frequencies of vibration of the atoms in a crystal about their positions of equilibrium. These modes and frequencies would be determined by the masses of the atoms and their interactions with the surrounding atoms in a domain the extent of which is limited by the range of the interatomic forces. It follows that considerations regarding wave-propagation and boundary conditions are not relevant to the problem.

A rigorous mathematical investigation of the theory of the propagation of waves in a general crystal consisting of p interpenetrating lattices of atoms on the basis of the classical mechanics shows that only in the limiting cases of the lowest frequencies of vibration is the group velocity of the waves identifiable with their phase velocity. With increasing frequency, the phase velocity and the group velocity diverge from each other, and the group velocity becomes zero for $(24p - 3)$ distinct frequencies, the nature of the atomic modes of vibration for these frequencies being identical to the $(24p - 3)$ normal modes of vibration of the structure of the crystal referred to earlier in this address. Thus, the investigation from the standpoint of the theory of wave-propagation and of classical mechanics leads to the same result, namely that these are the $(24p - 3)$ characteristic modes and frequencies of vibration of the structural units of which the crystal is composed.

We may put the matter a little differently by saying that while Einstein's theory identifies the thermal energy of a crystal with the quantized vibrational energy of immense numbers of oscillators having identical frequencies, Born's lattice dynamics identifies it with the quantized energy of immense numbers of wave-motions whose frequencies are all different. The two approaches are clearly irreconcilable, since in the one case, the vibration spectrum of the crystal consists of a set of discrete frequencies, while in the other, it is a continuous spectrum. That Born's approach to the specific heat problem is indefensible becomes evident when we remark that his "waves" are not normal modes and hence are incapable of enumeration.

6. The thermal properties of crystals

We shall now consider the application of the ideas indicated in the present address to the interpretation of the physical behaviour of crystals. The thermal properties may be considered first, since the nature of the thermal agitation plays a leading role in relation to them.

A familiar fact of experience is the extreme slowness with which heat diffuses through a solid. On the other hand, elastic waves travel through a solid with a velocity of some thousands of metres per second. It would be a formidable problem to explain such a fundamental difference in behaviour, if one were to identify thermal energy with wave-motion, as is done in the theories of Debye and Born. Such a paradox does not however confront us on the present view of the nature of the thermal agitation in which it is identified with the energy of vibration of individual oscillators localised in the crystal. The conduction of heat through a solid would on this view be the result of an exchange of energy quanta between the individual oscillators. Such a process would bear no resemblance whatever to wave-propagation in the ordinary sense of the word.

The evaluation of the specific heats of crystals as a function of temperature reduces itself to the problem of determining the $(24p - 3)$ characteristic frequencies of atomic vibration. When p is unity or a small integer, the $21p$ superlattice frequencies make important contributions to the thermal energy. When p is large, however, the $(3p - 3)$ modes and frequencies of the unit cell reappear with only minor changes as superlattice modes and frequencies, and hence many of the latter could be identified with the former without sensible error in the calculation of the thermal energy; a considerable simplification thereby results. The thermal energy represented by the three translations of the supercell may be assumed to be proportional to the absolute temperature, except at the very lowest temperatures where its continuous spectrum of frequencies would have to be explicitly taken into consideration.

Crystals exhibit a surprising variety of behaviour in respect of the changes in their linear dimensions with rise or fall of temperature. The present view of the nature of thermal agitation which regards it as a localised vibration of individual oscillators opens a pathway to the interpretation of the observed facts. The finite amplitudes of vibration of the individual oscillators and the mechanical anharmonicity associated therewith would result in the frequencies of vibration diminishing in the higher states of excitation. It would also result in a change of the average dimensions of the individual oscillators, which again would depend on the modes of vibration and hence may be very different in different directions. The integrated effect would be a shifting accompanied by a broadening of the lines in the vibration spectra and a change in the linear dimensions of the crystal. Thus, a close correlation is to be expected between the thermal expansion of crystals and the changes in their spectroscopic behaviour with rise or fall of temperature.

7. The spectroscopic behaviour of crystals

The vibration spectra of crystals are accessible to experimental study with a great variety of materials and by diverse techniques of investigation. The nature of the

spectra becomes manifest when the absorption of light by crystals exhibiting visible colour (e.g., the inorganic chromates), or of ultra-violet light by crystals (e.g., the aromatic organic compounds) is investigated with the crystals cooled down to the lowest possible temperatures. The absorption spectra then appear fully resolved into a set of sharply defined lines. These can be interpreted as combinations of the electronic with the vibrational frequencies of the crystal. Very low temperatures are also necessary for effecting a similar resolution into sharp lines of the luminescence spectra of various crystals of which such luminescence is an inherent property, e.g., the uranyl salts and of other crystals of which the luminescence is ascribable to the presence of an impurity phosphor (e.g., ruby). Such luminescent crystals also exhibit at low temperatures characteristic absorption spectra which are resolved into discrete lines and which are related by an approximate mirror image symmetry to their emission spectra.

There are also other and rather more direct methods of investigation. Three different techniques based on infra-red spectroscopy are available, viz., the emission, absorption and reflection of infra-red radiations by crystals. In these techniques, the disturbing effects of thermal agitation and of the anharmonicity of the vibrating electric doublets in the crystal are strongly manifested. Nevertheless, by an appropriate choice of the material to be investigated and of the techniques used, e.g., by varying the thickness of the crystal, cooling it to low temperatures and the application of adequate resolving power, it is possible to obtain results capable of unequivocal interpretation. Finally, we have the method based on the study of the scattering of light in crystals. The results obtained by this method are of such importance that they will be considered separately in the next section.

The whole body of experimental evidence forthcoming with the materials and methods described above confirms the thesis that apart from disturbing effects such as those mentioned earlier, the atomic vibrations in crystals appear as a set of sharply defined monochromatic frequencies in the spectrum.

8. The scattering of light in crystals

The nature of the results to be expected when a crystal is traversed by an intense monochromatic beam of light is different in relation to the $(3p - 3)$ modes of atomic vibration which have the same phase in adjoining cells of the lattice, and the $21p$ modes in which the phases are opposite in adjoining cells along one, two or all three of the axes of the lattice. In either case, we are concerned with the scattered radiations having their origin in the changes of optical polarisability of the vibrating atomic groups. Ordinarily, except in the case where the symmetry of the vibrational modes results in there being no resultant change of optical polarisability, the $(3p - 3)$ modes would manifest themselves as frequency shifts in

the spectrum of the scattered light. On the other hand in the $21p$ modes, the optical moments being in opposite phases in adjoining cells, their effects would cancel out. However, if the amplitudes of vibration are sufficient, the changes in optical polarisability proportional to the squares of the atomic displacements would also have to be considered. It is then possible for all of the $(24p - 3)$ modes of atomic vibration to appear with double frequency shifts in the spectrum of the scattered light. The intensity of such scattering, being proportional to the square of the absolute atomic displacements, would necessarily be small. Strongly exposed spectrograms would accordingly be necessary to record the same.

It is evident that the study of the second-order spectra of light-scattering is of the greatest importance, since in the first place they allow us to observe and measure the frequencies of modes which do not appear in the first-order spectrum and secondly because the intensity of the lines of the second-order spectra relative to those of the first-order spectra is a measure of the absolute magnitude of the interatomic displacements responsible for the changes in optical polarisability. Studies of this kind are obviously most suitably undertaken with crystals of relatively simple structures, as for example, diamond, rock-salt, calcite and quartz, since the results are then most readily interpreted.

Very detailed investigations of the kind indicated carried out at Bangalore have established that the vibration spectra of crystals include both the $(3p - 3)$ and the $21p$ modes with discrete monochromatic frequencies, and further that the oscillators whose vibrations manifest themselves as frequency shifts are of the same order of magnitude in their dimensions as the unit cells of the crystal structure. The latter result is inferrable from the fact that the relative intensity of the first- and the second-order spectra is of the same order of magnitude in crystals as in fluids. For, the size of the quantized oscillators emitting the scattered radiation of any given frequency determines the absolute magnitude of the interatomic displacements responsible for the variations of optical polarisability.

Summary

1. Einstein's view of a crystal as an assembly of immense numbers of quantized oscillators having a common set of vibration frequencies is not only the logical and correct view of the matter but also proves itself when fully developed to be an eminently successful view. It gives us a deep and quantitative insight into the thermal behaviour of solids. The nature of the vibration spectra of crystals indicated by it is confirmed in detail by the results of spectroscopic studies with diverse materials and by various techniques and with especial completeness by studies on the diffusion of light in crystals.
2. The ideas underlying the specific-heat theories of Debye and Born are irreconcilable with the observed spectroscopic behaviour of crystals and especially with the effects exhibited in their second-order spectra of light-scattering.

The specific heats of crystals—Part I. General theory

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1. Introduction

The quantum theory of the specific heats of crystals proposed by Einstein in the year 1907 regards a crystal as an assembly of an immense number of harmonic oscillators with specific frequencies, the energy of vibration of which obeys the quantum rule; these oscillators form a system in thermodynamic equilibrium of which the behaviour can be described statistically with the aid of Boltzmann's theorem. Einstein identified these oscillators with the structural units ("Elementargebilde") in the crystal and assumed that they could be grouped into sets, each set comprising a great number of oscillators characterised by a common frequency of vibration; the total number of oscillators of all sorts is taken to be thrice the number of atoms comprised in the crystal. He showed it to be a consequence of his theory that the thermal properties of a crystal would stand in the closest relationship with its spectroscopic behaviour.

The assumptions on which Einstein's theory rests are clearly justified by the physical facts of the case. For, every crystal consists of an immense number of structural units similar to each other which are capable of mechanical vibration and which by reason of their similarity may be expected to exhibit identical dynamical behaviour. The theory is, in effect, a synthesis of the results indicated by classical dynamics for such a system with the notions of the quantum theory and the basic principles of thermodynamics. It involves no inherent contradictions and can therefore claim to be a rational approach to the fundamental problems of crystal physics. The following questions, however, need to be answered before any use can be made of the theory. How are the oscillators of different sorts envisaged in the theory related to the known structure of a crystal? How are they to be enumerated? What is the procedure by which the characteristic frequency of each set of oscillators may be evaluated? The present memoir concerns itself with finding the answers to these questions and thus giving form and substance to the ideas of a very general nature put forward by Einstein.

2. The normal vibrations of crystal structures

That the specific heat of a crystalline solid tends with rising temperature to reach a limiting value proportional to the number of atoms comprised in it is a clear indication that the theoretical approach to any explanation of the facts has of necessity to consider the subject from an atomistic standpoint. We have also to recognize the existence of interatomic forces; hence, the movements with which we are concerned are not simple translations of the individual atoms but vibrations of the atoms about their positions of equilibrium in the structure of the crystal. Any attempt to describe these vibrations or to enumerate them has necessarily to be based on the fundamental theorem in classical mechanics which states that all the possible small vibrations of a connected system of particles about their positions of equilibrium are summations of an enumerable set of normal modes; in each such normal mode the particles of the system have all the same frequency and the same or opposite phases of vibration. Hence, any rational approach to the specific heat problem must of necessity start with a consideration of the normal modes of vibration—in the sense of the theorem just stated—of the atoms about their positions of equilibrium in the lattice structure of the crystal.

The basic principle of crystal architecture is that the structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes into two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following a unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed and the normal mode therefore remains the same following the unit translation. Since these two alternatives are possible for a unit translation along each of the three axes of the lattice, we have $2 \times 2 \times 2$ or 8 possible situations. Considering each of these situations separately, we proceed to write down the equations of motion of the p atoms comprised in the unit cell in terms of $3p$ co-ordinates which determine their displacements. Since the displacements of the equivalent atoms in adjoining cells which interact with the atoms in the cell under consideration are also the same, the $3p$ equations of motion of the latter contain only $3p$ independent co-ordinates. They can therefore be completely solved, giving us $3p$ solutions for each of the eight possible situations referred to above. Thus in all, we have $24p$ solutions. $(3p - 3)$ of these solutions represent normal modes of vibration of the first kind, $21p$ solutions represent normal modes of the second kind and the three remaining solutions represent simple translations which have necessarily to be excluded.

The $(24p - 3)$ normal modes of vibration of the atoms in a crystal indicated by

the theory may be regarded as the modes of *internal* vibration of the group of $8p$ atoms comprised in a super-cell of the crystal lattice whose linear dimensions are twice as large as that of the unit cell consisting of p atoms. The three omitted solutions would then represent the translations along each of the three axes of the crystal lattice of the whole group of $8p$ atoms included in the super-cell. Thus, we recognise that the structural unit whose dynamical behaviour is representative of the entire crystal is not the unit cell of the crystal structure, but has twice its dimensions along each of the three axes of the lattice.

Thus, following Einstein, we may regard a crystal as an assembly of $(24p - 3)$ sets of oscillators, each of the sets having its own distinctive frequency of vibration. The number of oscillators in each set is the same as the number of super-cells containing $8p$ atoms which are included in the whole crystal. Each set of oscillators forms an assembly in thermodynamic equilibrium and its behaviour can therefore be described statistically with the aid of Boltzmann's theorem. The average energy of an oscillator in each set is given by Einstein's formula for the particular frequency. Multiplying this by the number of super-cells contained in the volume of the crystal, we obtain an expression for the energy of all the oscillators in that set. Finally, summing up the expressions thus obtained for all the $(24p - 3)$ sets with their respective frequencies of vibration, we obtain an expression for the thermal energy arising from the excitation of the vibrations of the atoms having precisely specifiable frequencies.

3. The vibration spectra of crystals

The foregoing results may be summed up as follows. If a unit volume of the crystal contains S super-cells each including $8p$ atoms, the total number of degrees of atomic freedom is $24pS$; a very large proportion of this number, viz., $(24p - 3)S$ degrees of freedom, appears in the vibration spectrum of the crystal as sharply defined monochromatic frequencies; $(3p - 3)$ of these frequencies represent vibrations in which equivalent atoms contained in each super-cell have the same amplitudes and phases of vibration, while the $21p$ other frequencies represent modes of vibration in which the amplitudes are the same but the phases are opposite for equivalent atoms along one, two or all three of the axes of the lattice.

We have now to consider and determine the nature of the movements represented by the $3S$ degrees of atomic freedom left out in the preceding enumeration. This is also the number of degrees of freedom of translation of the S super-cells included in the crystal. Any translation of an individual super-cell would necessarily set up forces resisting such movement and also tending to displace neighbouring super-cells. We are therefore led to assume that the $3S$ degrees of freedom under discussion would manifest themselves as internal modes of vibration in elements of volume of larger dimensions than our super-cell. The larger such element of volume is, the lower would be the limit of the possible

frequencies of such vibration. The translations of the individual super-cells are therefore to be associated with a whole series of frequencies lying between zero and an upper limit which is set by the frequency of internal vibrations in our super-cell. To take account of the anisotropy of the crystal, we would, in general, have to assume separate upper limits of frequency for the translations along the three axes of the crystal. It is left to determine how the $3S$ unassigned degrees of freedom are distributed amongst the oscillators of various frequencies lying in the permitted ranges $0 \rightarrow \nu_x, 0 \rightarrow \nu_y, 0 \rightarrow \nu_z$.

The problem indicated above can be dealt with and solved in a very simple manner. Consider two volume elements in the crystal which have the same shape as our super-cell and whose dimensions are respectively m and n times larger. The number of degrees of freedom of translation of these enlarged super-cells is respectively three times the number of such cells included in the volume of the crystal; the difference between them, viz., $3S(1/m^3 - 1/n^3)$ would therefore be the number of oscillators whose frequencies lie between ν_m and ν_n which are respectively their lowest frequencies of internal vibration. But the principle of dynamical similarity enables us to write $\nu_m = k/m$ and $\nu_n = k/n$ where k is a constant having the dimensions of a frequency. Hence, as m approaches n , $\nu_m - \nu_n$ may be set equal to dv and the number of oscillators whose frequencies lie between ν_m and ν_n may be written as $9S \nu^2 dv/k^2$. On integrating this between zero and ν_l (the upper limit of the permitted frequencies), we should recover $3S$ as the total number of oscillators, and hence k^3 is identified as ν_l^3 . Accordingly, the law of distribution of frequency in the spectrum may be written as $9S \cdot \nu^2 dv/\nu_l^3$ for the isotropic case. More generally, for an anisotropic crystal ν_l may be replaced by ν_x or ν_y or ν_z respectively for the three directions of translations and the numerical factor 9 is replaced by 3.

The law of distribution of the frequencies thus derived indicates that the majority of the oscillators now under consideration have frequencies not far removed from the upper limit. The same result may be expressed otherwise by the statement that the majority of the oscillators are of very small dimensions not far removed from the lower limit, namely the dimensions of the super-cell. If, for example, we were to identify *all* the vibrations arising from the translations of the super-cell with the internal vibrations in a volume element whose dimensions are *twice* those of the super-cell, we would not be seriously in error. All except one-eighth of the $3S$ degrees of freedom would be accounted for in such an enumeration; the residue omitted would represent oscillations in still larger volume elements appearing with still lower frequencies.

4. The thermal energy of crystals

The atomistic approach to the specific heat problem proposed by Einstein, when fully developed, thus leads us to the following picture of the nature of the

vibrations in a crystal which are the carriers of the thermal energy. The oscillating units are *not* the unit cells of the structure, but are twice as large as the unit cells in their linear dimensions; their oscillations are of two kinds, namely, those arising from their internal vibrations and those arising from their translatory movements. The oscillations of the former description appear with $(24p - 3)$ discrete frequencies of vibration, p being the number of atoms contained in the unit cells of the crystal structure. The translatory movements, on the other hand, appear with a spectrum of frequencies all of which are lower than those of the internal vibrations. These, for the most part, are concentrated near the upper limit of their permitted range; but there is a residue which tails off as a continuous spectrum to very low frequencies.

Accordingly, making use of the reasoning employed by Einstein for evaluating the average energy of an oscillator in each of the sets under consideration, we obtain the following expression for the heat content of a volume of a crystal containing N unit cells of the crystal structure as a function of the temperature, namely

$$\frac{N}{8} \left[\sum_{i=1}^{24p-3} \frac{h\nu_i}{e^{h\nu_i/kT} - 1} + \frac{3}{v_l^3} \int_0^v \frac{3h\nu^3 d\nu}{e^{h\nu/kT} - 1} \right].$$

The numerical factor $1/8$ appears in the expression because each dynamic unit contains 8 unit cells of the crystal structure. On differentiating the expression with respect to T as usual, we get the formula for the specific heat.

The following remarks may be made regarding the numerical evaluation of the expression given above. All the $(24p - 3)$ frequencies would be distinct from each other only in the case of a completely anisotropic crystal. If any symmetry elements are present, the number of distinct frequencies would be naturally diminished and the formula would then contain only such smaller number, but the individual terms would then have to be multiplied by their respective degeneracies. Such reduction in the number of distinct frequencies would naturally appear both in respect of the $(3p - 3)$ frequencies in which both the amplitudes and the phases are the same in adjacent unit cells and in the $21p$ others in which the phases may be opposite as already explained. As an illustration of these remarks, we may consider a case in which $p = 2$ and the crystal belongs to the cubic class and its structure consists of two interpenetrating face-centred cubic lattices. The $(3p - 3)$ distinct frequencies then reduce to a single triply degenerate frequency; the $21p$ or 42 other vibrations reduce to only eight distinct frequencies, all of which may be readily described in geometric terms related to the structure of the crystal.

Since the first term in the expression for the thermal energy is a summation extended over $(24p - 3)$ distinct modes of vibration, while the second represents only the three residual translations, it is evident that the latter would be of very minor importance relatively to the first, especially in those cases where p is very large, in other words when the crystal has a multi-atomic structure. The position

is a little different when p is small, as for example, when p is equal to 1. The contribution from the second term would not then be altogether negligible in comparison with the first term. The second term also acquires some importance relatively to the first at very low temperatures. For, since the frequencies appearing in it are low, their contributions to the specific heat would survive when those due to the vibrations of the higher frequencies appearing in the first term have been effectively frozen out by reason of Boltzmann's theorem.

5. The spectroscopic behaviour of crystals

In his paper of 1907, Einstein emphasised the intimate relationship indicated by his theory between the thermal properties of crystals and their optical behaviour. It is appropriate therefore that we make a reference here to the decisive support given to the results of the theory set forth above by the experimental facts regarding the spectroscopic behaviour of crystals revealed by investigations made with a great variety of materials and by diverse techniques of investigation. We need not however dilate on this topic, since the experimental situation in this respect has been reviewed in my Lindau address, and since, moreover, the particular case of the diamond which illustrates the general principles in a very striking fashion has been dealt with in detail in a recent lecture published in these *Proceedings*.

6. Summary

In Einstein's atomistic approach to the specific heat problem, a crystal is regarded as an assembly of sets of individual harmonic oscillators, each set consisting of a great number of oscillators having a common frequency of vibration. In the present paper, this view is developed and an expression is obtained for the thermal energy of the crystal which appears as a summation of $(24p - 3)$ terms arising from the individual monochromatic frequencies of internal vibration of the dynamic units of the crystal structure each containing $8p$ atoms, with a supplementary term which takes account of the translational movements of the same units manifesting themselves as a continuous spectrum of frequencies of vibration within the crystal.

The specific heats of crystals—Part II. The case of diamond

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In a lecture on the diamond published in the September issue of these *Proceedings* (vol. 44, 1956, p. 99), the vibrations of the diamond structure were discussed in detail and the results of spectroscopic investigations on the nature of the vibration spectrum were also set forth. The results contained in that paper furnish us with all the material necessary for a complete theoretical evaluation of the specific heat of diamond over the entire range of temperatures for which experimental data are available. We shall now proceed to make such an evaluation and compare it with the results of the published measurements on the specific heat of diamond.

Table 1 gives a list of the nine characteristic frequencies of the diamond structure expressed in wave-numbers (cm^{-1}), their respective degeneracies and the geometric description of the corresponding modes of vibration. The frequencies shown in the last column of the table were evaluated with the aid of the equations of motion and a set of force constants and were also independently confirmed by the results of spectroscopic investigation by several different techniques. It is a simple matter with the aid of the table to calculate the contributions to the specific heat arising from the nine modes of internal vibration of the diamond structure. The lowest frequency appearing in the table expressed in wave-numbers, viz., 621 cm^{-1} may also be properly assumed to be the upper limit of frequency in the continuous spectrum of the vibrations arising from the translations of the super-cell of the crystal structure, as explained in part I of the present paper.

The contribution to the specific heat arising from the continuous part of the vibration spectrum can be readily evaluated on this basis with the aid of the tabulated values of the relevant functions available in “Landolt–Bornstein”. Table 2 below shows the results of such computations. The contributions to the atomic heat arising respectively from the discrete spectrum and from the continuous spectrum are shown separately for a series of temperatures ranging from 15° to 1100° on the absolute scale. The sum of the two contributions is also tabulated.

Table 1. Vibration spectrum of diamond

No.	Degeneracy	Description of the mode	Frequency in cm^{-1}
I	3	Oscillation of the two interpenetrating lattices against each other	1332
II	8	Tangential oscillation of the octahedral planes	1250
III	6	Tangential oscillation of the cubic planes	1239
IV	4	Normal oscillation of the octahedral planes	1149
V & VI	(3 + 3)	Normal oscillation of the cubic planes	1088
VII	4	Normal oscillation of the octahedral planes	1008
VIII	6	Tangential oscillation of the cubic planes	740
IX	8	Tangential oscillation of the octahedral planes	621

Table 2. Theoretical computation of the atomic heat of diamond
(Calories per gram-atom per degree)

Absolute temperature T°	Discrete frequencies	Continuous spectrum	Total	Absolute temperature T°	Discrete frequencies	Continuous spectrum	Total
15	—	0.00014	0.00014	200	0.4069	0.1631	0.5700
20	—	0.00033	0.00033	225	0.5894	0.1895	0.7789
25	—	0.00064	0.00064	250	0.7844	0.2124	0.9968
30	—	0.0011	0.0011	275	1.0137	0.2319	1.2456
40	—	0.0026	0.0026	300	1.2418	0.2486	1.4904
50	—	0.0051	0.0051	350	1.700	0.275	1.975
60	—	0.0088	0.0088	400	2.139	0.294	2.433
70	0.0005	0.0140	0.0145	450	2.538	0.308	2.846
80	0.002	0.0207	0.0227	500	2.892	0.319	3.211
90	0.0056	0.0290	0.0346	600	3.469	0.334	3.803
100	0.0128	0.0388	0.0516	700	3.899	0.344	4.243
120	0.0419	0.0619	0.1038	800	4.224	0.350	4.574
140	0.0957	0.0877	0.1834	900	4.465	0.355	4.820
160	0.1758	0.114	0.2898	1000	4.653	0.358	5.011
175	0.2517	0.1333	0.3850	1100	4.797	0.360	5.157

The values of the atomic heats of diamond listed in table 2 are exhibited in graphical form in figure 1. At temperatures below 70° absolute, the curve appears to touch the axis since the very low values of the specific heats in this region cannot be represented on the scale of the graph. The values in this region are, however, of great interest, since, as will be seen from table 2, they arise exclusively from the contribution of the continuous spectrum of frequencies which represents only 3 out of the 48 degrees of atomic freedom of movement of the crystal. Accordingly, the theoretical curve for this part of the temperature range has been drawn with a greatly enlarged scale for the ordinates in figure 2 below. Fortunately also, the specific heat of diamond in this region of temperature has been the subject of detailed investigation of Warren DeSorbo (*Journal of Chemical Physics*, vol. 21, 1953, p. 876) and his experimental results for this very interesting region are plotted in the diagram. A gratifying agreement between theory and observation will be noticed.

The specific heat of diamond in the range of absolute temperatures from 70° to 300° was determined by K S Pitzer (*Journal of Chemical Physics*, vol. 6, 1938, p. 68). The measurements by DeSorbo also cover this range. A careful inter-comparison between them shows that Pitzer's values are distinctly higher than those of DeSorbo throughout this range and that they also exhibit a scatter which is distinctly larger than the results of DeSorbo. DeSorbo's work is of later date and his data form a continuous sequence over a wider range of temperatures. For these reasons, it was felt that a comparison between theory and experiment would be more appropriately made with the result of DeSorbo. Figure 3 below shows such comparison and here again a very satisfactory agreement emerges.

Finally, figure 4 exhibits a comparison between the theoretical values and the experimental data in the temperature range from 300° to 1100° absolute covered

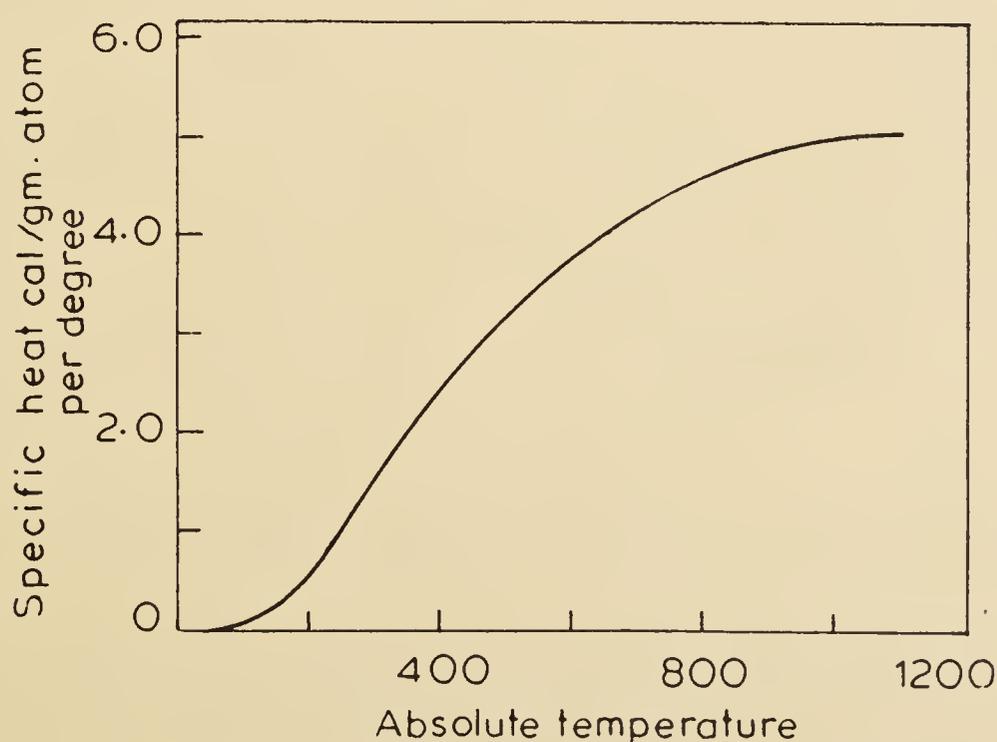


Figure 1. The atomic heats of diamond calculated from the spectroscopic data.

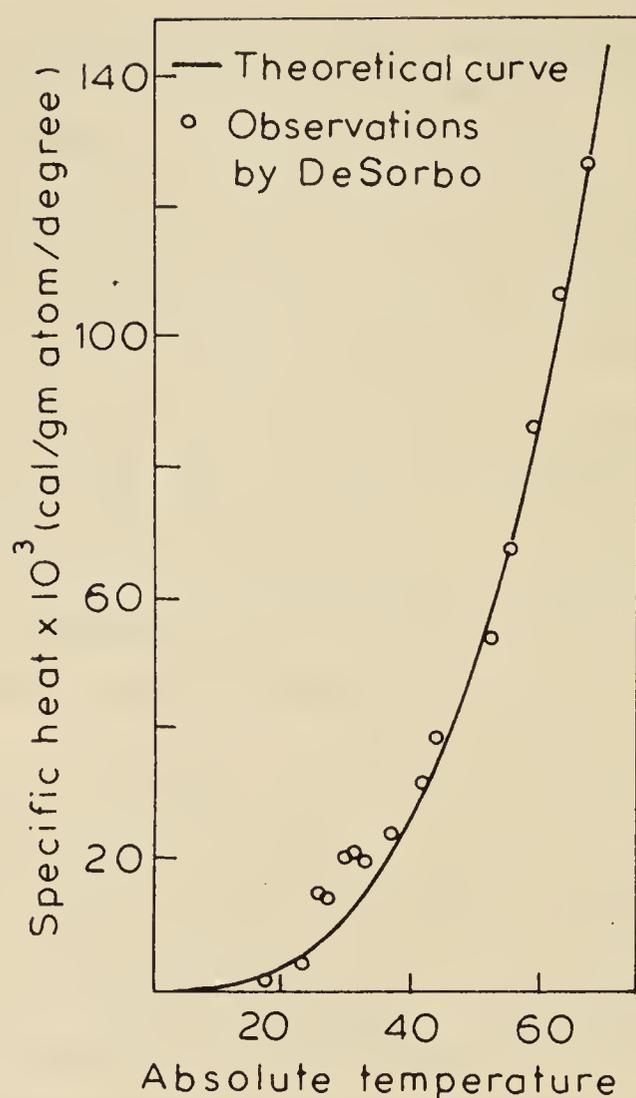


Figure 2. Comparison between theory and experiment at very low temperatures.

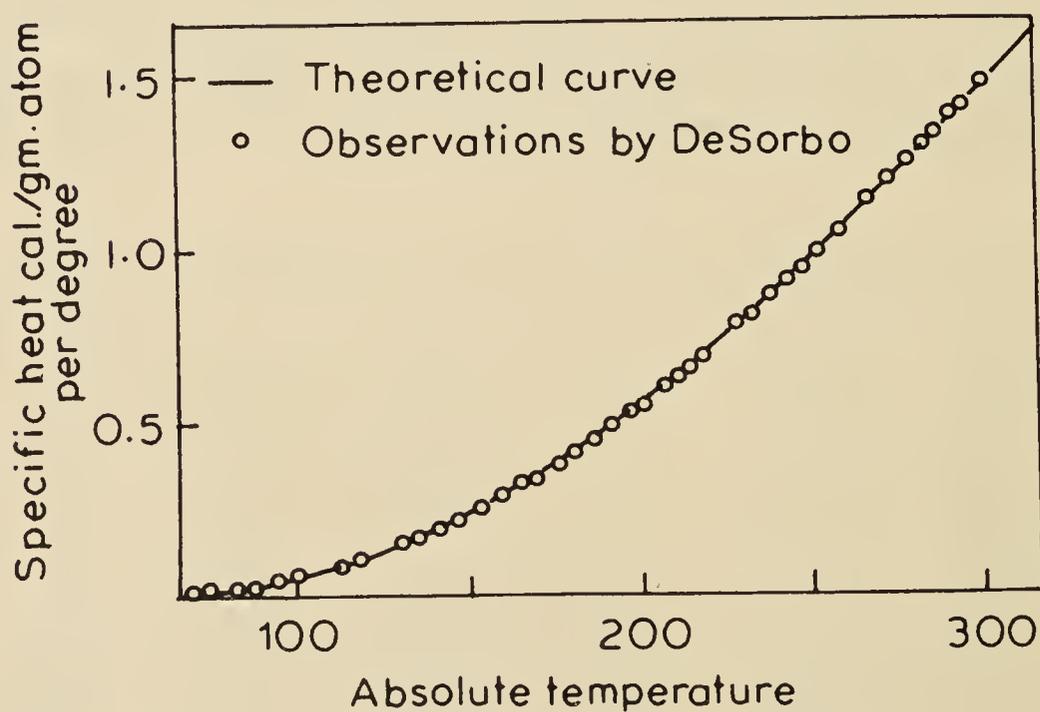


Figure 3. Comparison of theory and experiment below room temperature.

by the determinations of Magnus and Hodler (*Annalen Der Physik*, vol. 80, 1926, p. 808). The observed discrepancies throughout the range do not exceed two per cent and in most cases are much less. The agreement should therefore be considered as satisfactory.

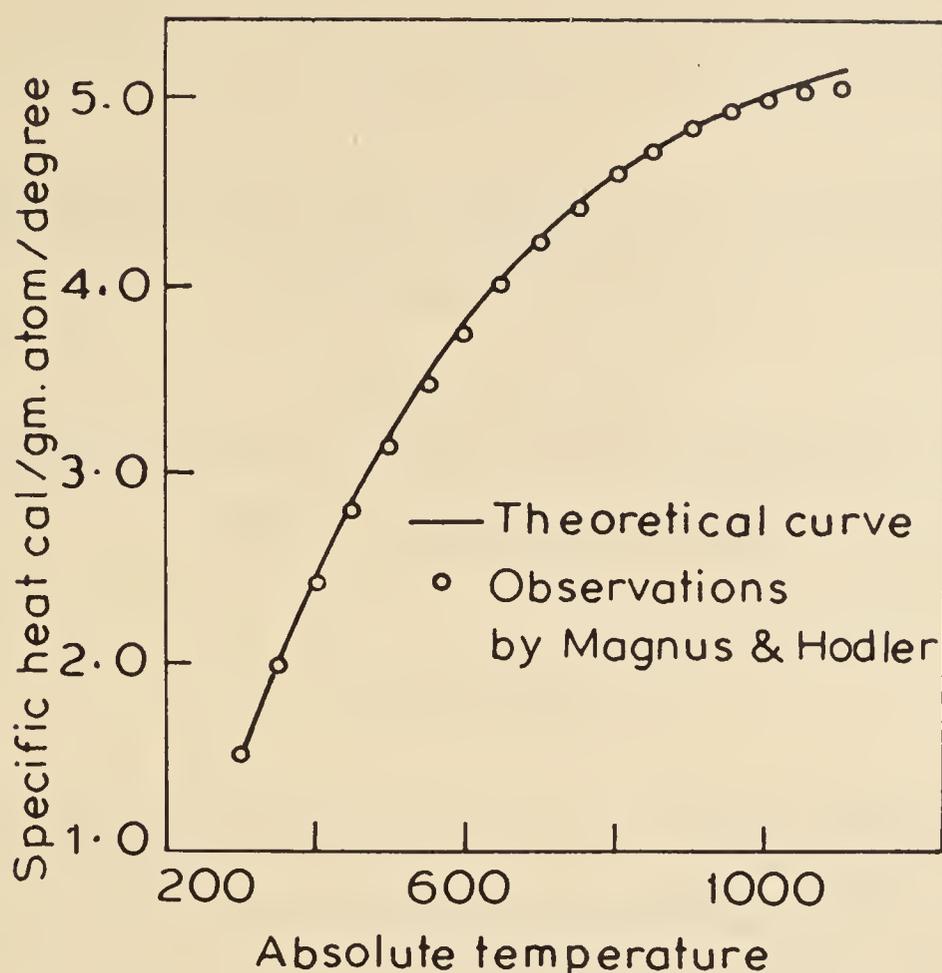


Figure 4. Comparison between theory and experiment at high temperatures.

Summary

The specific heat of diamond in the temperature range between 15° and 1100° absolute has been computed theoretically, making use of the nine spectroscopically determined vibration frequencies of the diamond structure as well as their known degeneracies, and further taking the lowest of these nine frequencies to be the upper limit of frequency in the residual continuous spectrum as explained in part I of the paper. The results are compared with the experimental observations of DeSorbo from 15° to 300° absolute and of Magnus and Hodler from 300° to 1100° absolute. A highly satisfactory agreement between theory and experiment emerges.

The specific heats of crystals—Part III. Analysis of the experimental data

SIR C V RAMAN

Memoir No. 91 from the Raman Research Institute, Bangalore-6

Received November 29, 1956

1. Introduction

A theory of the specific heats of crystals has been put forward in part I of this series of papers which is based on the determination and enumeration of the normal modes and frequencies of vibration of the atoms in the crystal about their positions of equilibrium. The theory enables the thermal energy of a crystal to be expressed as a function of the temperature in terms of these frequencies. Diamond is admirably suited for a test of the theory, since the frequencies of vibration of the atoms in its structure may be evaluated theoretically and the same frequencies also admit of precise measurement by several different spectroscopic techniques. The specific heat of diamond can accordingly be determined in terms of these frequencies over the whole range of temperatures for which reliable data are available. As has been shown in part II of this series of papers, the theory emerges triumphantly from the test, its results being in complete accord with the results of the spectroscopic investigations on the one hand and with the measured specific heat data on the other.

In the present memoir we shall consider the converse problem of deducing the nature of the atomic vibration spectrum for a given crystal from the empirically determined specific heat data. The method adopted for this purpose may be briefly stated here. We assume that all the atomic oscillators in the crystal have a common frequency of vibration and calculate from the observed specific heat at any given temperature what that frequency is. The frequency thus evaluated itself appears as a function of the temperature, and a graph showing its variation over the entire range of temperature gives us a useful indication of how the total number of degrees of atomic freedom is distributed over the entire range of frequencies covered by the atomic vibration spectrum of the crystal. The results obtained by this procedure and their significance are best understood by considering an actual example. We shall apply the method to the analysis of the specific heat data for diamond and show how useful conclusions may be derived therefrom.

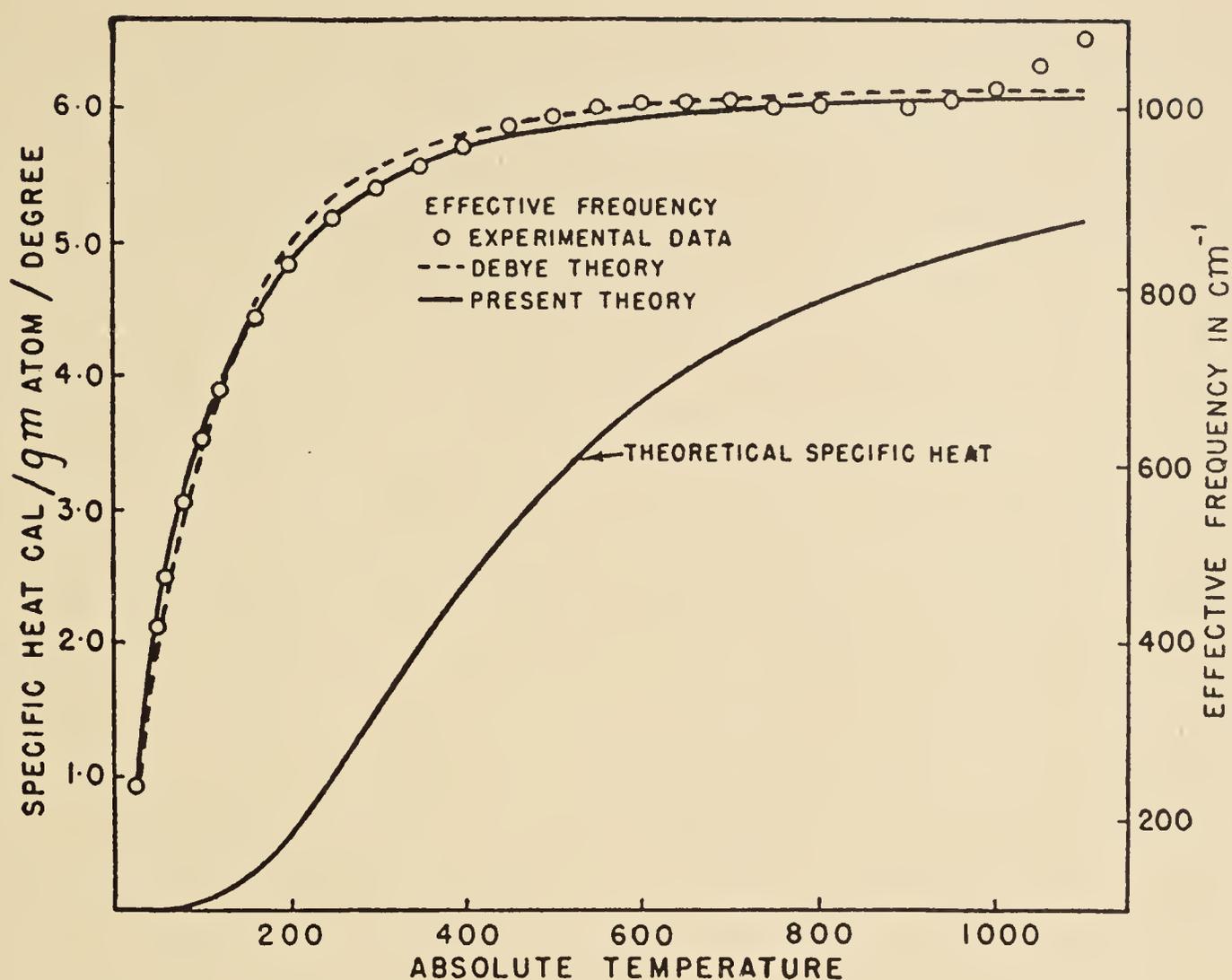


Figure 1. Analysis of the specific heat of diamond.

2. Analysis of the specific heat curve

In figure 1 above, we reproduce the graph of the specific heat of diamond as a function of the temperature deduced from the spectroscopic data in part II of the present series of papers. The abscissae in the figure are the absolute temperatures, while the ordinates give the calculated specific heats, the scale for the same appearing on the left-hand side of the figure. Taking the value of the specific heat given by this graph for any given temperature and with the aid of a table of Einstein's specific heat function, a frequency of vibration is found which, if ascribed to all the atomic oscillators in the crystal, would give that value for the specific heat at that temperature. We may call the frequency thus evaluated the *effective average* of the atomic vibration frequencies at that temperature. A graph showing how this effective frequency varies with the absolute temperature appears in figure 1 as a continuous curve; the scale of frequencies is that shown on the right-hand side of the figure. It will be seen that the graph is practically a horizontal line at the highest temperatures, the frequency having the value 1016 cm^{-1} at 1100° ; it then drops very slowly, being 1013 at 1000° , 1006 at 800° , and 992 at 600° K . Thereafter, it falls a little more quickly, being 978 at 500° , 954

at 400° , 911 at 300° , 826 at 200° and 767 at 160° . At still lower temperatures, the frequency drops down steeply and at 25° reaches the value 247 cm^{-1} .

The course taken by the frequency-temperature curve is readily understood if we recall the features exhibited by Einstein's specific heat function for various values of the argument; the function vanishes for large values of the argument, while for small values it reaches a limit in the vicinity of which the function does not vary appreciably with the argument; intermediately, however, the function decreases progressively as the argument increases and at an approximately uniform rate. The specific heat curve which we have analysed was obtained by the summation of a set of Einstein functions with different arguments, giving them fractional weights proportionate to the number of oscillators having the particular frequencies. In these circumstances, the "effective average frequency" deduced in the manner explained would necessarily vary with the temperature; at high temperatures, the "*effective average frequency*" would be the same as the *arithmetical average of the frequencies multiplied by their respective weights* but with the very lowest frequencies excluded in casting the average. At moderately high temperatures, the effective average would continue to approximate to the arithmetical average, but if the temperature be so low that the Einstein functions for some of the higher frequencies become vanishingly small, it would show a marked fall and finally, when all the higher frequencies have dropped out in the summation, it is the few surviving oscillators with the lowest frequencies that would determine the effective average frequency. The latter would then be necessarily very small.

The specific heat curve appearing in figure 1 was derived from a set of Einstein functions representing monochromatic frequencies whose values and respective degeneracies are the following: 1332(3), 1250(8), 1239(6), 1149(4), 1088(6), 1008(4), 740(6) and 621(8) and, in addition, a residual continuous spectrum with a weight three. The arithmetical sum of all these vibration frequencies multiplied by their respective degeneracies and divided by the total of 48 is 987 cm^{-1} . If, however, we omit the continuous spectrum and take the arithmetical average after division by 45, we obtain 1022 cm^{-1} as the arithmetical average frequency. This is nearly the same as the value of the effective average frequency at 1100° which is 1016 cm^{-1} . The course of the graph in the middle ranges of temperature is determined by the relative weights of the different frequencies. It will be noticed that these weights are distributed in a more or less uniform manner over the entire range from 1332 cm^{-1} to 621 cm^{-1} . It is this feature which is responsible for the graph of the effective frequency dropping quite gradually from 978 cm^{-1} to 767 cm^{-1} in the temperature range between 500° and 160° .

3. Comparison with the observations

As has already been shown in part II of this series of papers, a highly satisfactory agreement emerges when the specific heat computed from the spectroscopic data

is compared with the values measured by DeSorbo in the temperature range from 40° to 300° and by Magnus and Hodler between 300° K and 1100° K. The same comparison may be made in a different manner, viz., by calculating from the observed specific heat at any temperature the effective average of the frequencies of the atomic oscillators and plotting them on the same graph as the effective average calculated from the theoretical specific heat curve. This has been done and the experimental values are shown as circles in figure 1. The specific heats from 40° to 300° were in the present instance taken from the table of smoothed means given by DeSorbo as best representing his determinations [*J. Chem. Phys.*, **21** 876 (1953)]. The experimental data from 300° upwards were those determined by Magnus and Hodler [*Annalen der Physik*, **80** 808 (1926)]. It will be seen that over the whole range of temperatures upto 400° the experimental values fall smoothly on the theoretical curve. Between 400° and 1000° the experimental values lie about the theoretical curve, but there are appreciable deviations of about $\pm 10 \text{ cm}^{-1}$. In this region of temperatures, this would correspond to variation in the specific heats of about 2 per cent of the measured values. These differences may be reasonably explained as due to inevitable errors in the determination of the specific heats at such high temperatures with small quantities of the material (10 grams).

4. Analysis of Debye's specific heat function

The values for the specific heat of diamond given by Debye's theory have been analysed in the same manner as that explained above and represented in figure 1 as a broken line. In making this calculation, the upper limit of frequency in the Debye integral has been taken to be 1332 cm^{-1} which is the spectroscopically observed highest fundamental frequency. This limiting frequency also fits the experimentally observed specific heats between 450° and 1100° with an accuracy of 1 per cent, the deviations being as often positive as negative. It should also be remarked that the limiting frequency calculated from the elastic constants of diamond comes out as 1304 cm^{-1} in fair agreement with the spectroscopic value of 1332 cm^{-1} .

Comparing now the continuous curve and the broken line appearing in figure 1, it will be seen that the latter lies entirely above the former in the temperature range from 1100° to 140° . The broken curve crosses the continuous curve at about 140° and lies below the latter down to the lowest temperatures.

This difference in the course of the two curves is highly significant. For, it indicates that between 140° and 400° , the Debye theory gives consistently lower specific heats than those actually observed, while between 40° and 140° , it gives higher specific heats than those observed. The actual specific heats, theoretical as well as those observed in these ranges, have been plotted in figures 2 and 3, as continuous and broken curves and as circles respectively, and exhibit this situation very clearly.

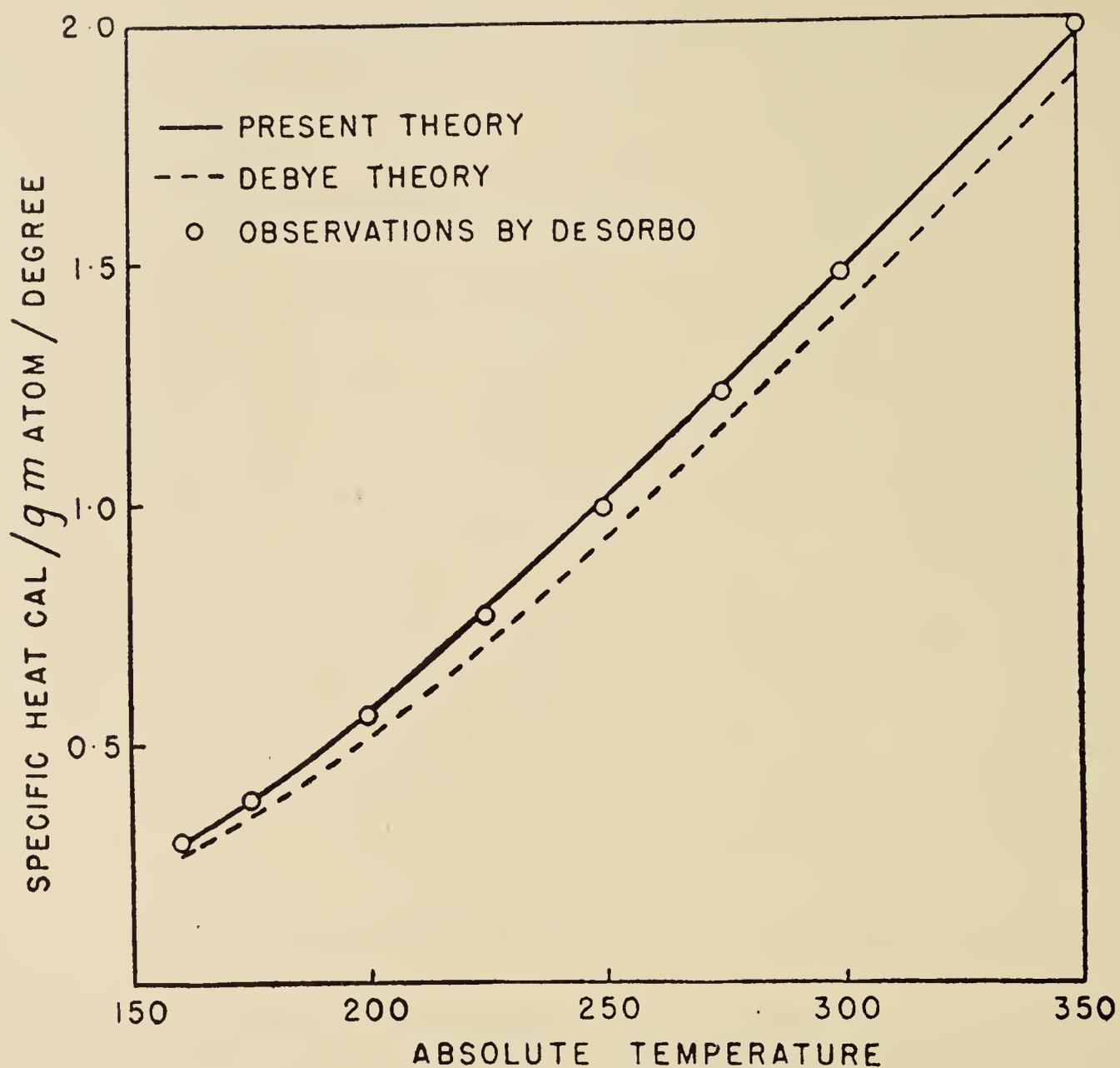


Figure 2. Specific heats of diamond.

5. Comments on Debye's theory

We shall now consider the theoretical implications which attach to the facts elicited by the foregoing analysis.

In the first place we remark that since the effective average frequency in the temperature range between 1100° and 500° lies close to 1000 cm^{-1} , any assumption whatever regarding the distribution of frequencies in the atomic vibration spectrum which gives us 1000 cm^{-1} as the effective average would fit the specific heat data satisfactorily within the limits of error of the experimental determinations. If, for example, we assume that all the atomic oscillators had a frequency of 1000 cm^{-1} , the calculated specific heat would agree with the observed values in that temperature range within one or two per cent. Likewise, if we assume that half the atomic oscillators have a frequency of 1332 cm^{-1} and the other half have the frequency 666 cm^{-1} thereby giving us an average frequency of 999 cm^{-1} , the specific heat data would also be fitted in that range with the same measure of accuracy. It follows that the agreement between the specific heat

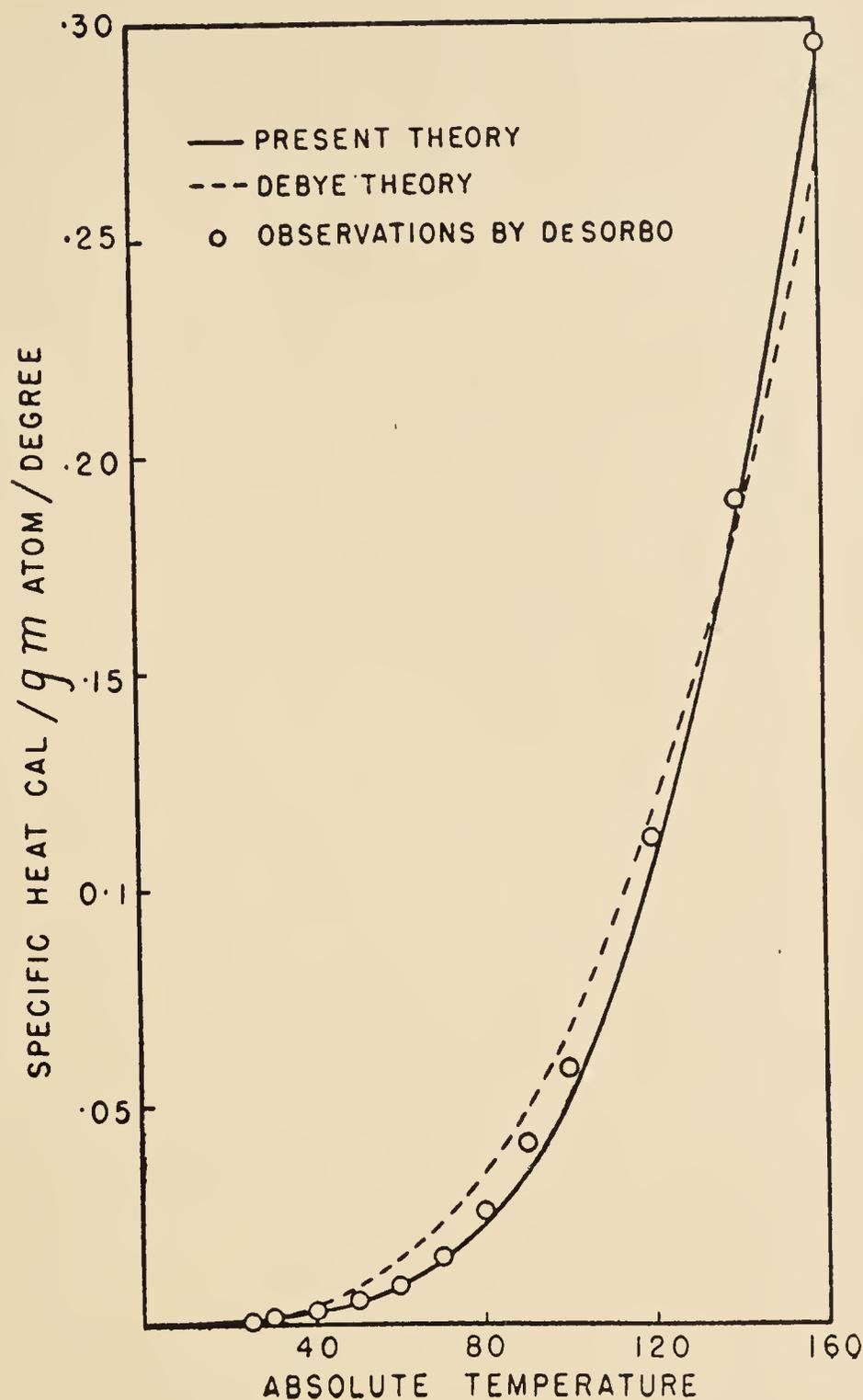


Figure 3. Specific heats of diamond.

theory of Debye and the experimental determinations in this temperature range only indicates that the distribution of frequencies assumed in that theory gives the arithmetical average of the frequencies more or less correctly. That is so, since the arithmetical average is three-fourths of the limiting frequency and is therefore 999 cm^{-1} .

The second remark we have to make is that the precise course of the specific heat curve in the middle range of temperatures, in other words, between 140° and 500° , is of the highest importance in enabling us to decide whether or not any assumed distribution of frequencies agrees with or differs radically from the actual distribution. It has already been remarked that in this range the Debye function gives systematically a lower specific heat than that observed, the

maximum deviation expressed as a percentage being about 10 per cent at about 200° K. The present analysis makes it clear that this difference arises because the distribution of the frequencies contemplated in the Debye theory differs radically from the actual distribution; instead of all the frequencies being densely crowded together near the upper end of the frequency range, they are actually distributed in a more or less uniform manner over a wide range of frequencies. It may be remarked that a deviation in the opposite sense, viz., with the calculated values higher than the observed ones, appears in the same temperature range if we assume that half the oscillators have a frequency of 1332 cm^{-1} and the other half a frequency of 666 cm^{-1} . This makes it clear that the actual distribution of frequencies does not involve a division of the atomic oscillators into two groups with such widely separated frequencies.

The third and the final remark that we have to make is in respect of the specific heats of diamond in the lowest part of the temperature range. The failure of the Debye theory to represent the course of the specific heat curve in this region is very conspicuous. A great many measurements were made by DeSorbo in this part of the temperature range and as he himself has pointed out, they deviate markedly from the course of the Debye function based on a constant limiting frequency. DeSorbo has exhibited this failure by drawing a graph representing the "characteristic Debye temperature" as a function of the temperature, and this exhibits a pronounced peak at 60°. As will be seen from our figure 3, the specific heat at this temperature given by the Debye theory assuming the limiting frequency to be 1332 cm^{-1} is 60 per cent in excess of the observed value.

Debye claimed in his original paper that the explanation of the behaviour of the specific heat of crystals at the lowest temperatures constituted the major success of his theory. Since, as we have seen, the theory actually fails most completely at these same low temperatures in the case of diamond, the only possible inference which can be drawn from the facts is that the identification of the thermal energy of crystals with the energy of stationary elastic vibrations in their interior on which the theory is based is a misconceived idea, in other words, that the theory itself is fundamentally untenable.

6. Summary

The functional dependence of the specific heat of a crystal on the temperature may with advantage be expressed as a variation with temperature of the effective average frequency of the atomic oscillators, the same being determined from the argument of the Einstein function which gives the observed specific heat at that temperature. The usefulness of this representation is shown in the paper by a detailed discussion of the experimental data for diamond. It emerges that the distribution of frequencies adopted in the Debye theory is irreconcilable with the observed course of the frequency-temperature curve. It is also pointed out that

the large excess which the specific heat calculated from that theory exhibits over the observed values in the region of low temperatures shows that the ideas on which that theory is based are misconceived and that the theory itself is untenable.

The heat capacity of diamond between 0 and 1000° K

SIR C V RAMAN

Memoir No. 103 of the Raman Research Institute, Bangalore-6

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1. Introduction

The evaluation of the heat capacity of diamond on the basis of the theory of specific heats of crystals advanced by the author formed the subject of a recent publication¹ in these *Proceedings*. Since then, fresh experimental determinations have been reported which go down to temperatures at which the value of C_p for diamond is as low as 0.0001, in other words only a fifty-thousandth part of its value 5.0 at 1000° K, which is itself smaller than the theoretical maximum of 5.96 for a monatomic solid. We proceed here to consider the new experimental results. The theoretical evaluation already published succeeds in explaining the change of C_p with temperature over the whole of this enormous range of values in a highly satisfactory manner, but with certain reservations made necessary by the fact that the theoretical calculations are based on the spectroscopic behaviour of ideal diamonds, whereas the reported determinations have been made with material which is very far indeed from being ideal. To exhibit the closeness of the agreement which is observed over practically the entire temperature range as well as the minor differences which are noticeable in certain limited parts of it, the data have plotted on adequate scales alongside of the theoretical values in a series of graphs which are reproduced in the present paper. The cause of the small differences which appear in the temperature range between 50 and 150° K is discussed and it is shown that they are explicable in terms of the differences in the spectroscopic behaviour of ideal and non-ideal diamonds.

Diamond illustrates in a most striking manner the fundamental relationship between the specific heats of crystals and their spectroscopic behaviour. Being an elementary solid crystallising in the cubic system with an exceptionally simple structure, the characteristic modes of atomic vibration which determine both the thermal behaviour and the spectroscopic properties of diamond can be described in geometric terms without any reference to the magnitude of the interatomic force constants. Considerations of a general nature enable us to go further and arrange these modes in a scale of descending frequency, thereby greatly facilitating their identification. Diamond being a transparent solid, the modes and frequ-

encies of atomic vibration in it are also accessible to observation by a variety of spectroscopic methods. It is found possible to determine these frequencies with precision and compare them with the theoretically computed values. Thus theory and experimental agree to give us a complete and detailed picture of the atomic vibration spectrum of diamond. It thereby becomes possible to evaluate the heat capacity of the crystal in a completely independent fashion involving no assumptions of any sort. The agreement which emerges between the results of such evaluation and the experimental data is a convincing demonstration of the correctness of the theoretical approach.

2. The vibration spectrum of diamond

The crystal structure of diamond consists of two distinct sets of atoms of carbon which appear separately in layers parallel to the faces of the octahedron and the cube respectively. The normal modes of atomic vibration of the structure can be readily described in terms of this arrangement. The principal mode of vibration is an oscillation of the two sets of atoms with respect to each other along any one of the three cubic axes and has therefore a degeneracy of 3. The atoms present in the layers parallel to the octahedral faces may oscillate with respect to each other either normally or transversely to themselves with degeneracies of four and eight respectively; but since the adjacent non-equivalent layers may oscillate either in the same or opposite phases, we have two such sets of modes. Likewise, we have two sets of modes in which the layers of atoms parallel to the cube faces oscillate normally or transversely to themselves with degeneracies of three and six respectively. Thus, we have 9 distinct normal modes with degeneracies of 3, 4, 4, 8, 8, 3, 3, 6 and 6 respectively, making a total of 45 modes in all. Considering the set of 16 atoms contained in a volume element which is twice as large in each direction as the unit cell of the crystal structure, the total number of atomic degrees of freedom of this group is 48. The 45 modes of vibration described above may be regarded as the *modes of internal vibration of this group*, while the three degrees of freedom left over represent *its three translations*.

In a lecture on the diamond delivered at Zurich, Freiburg and Bonn in July 1956, and subsequently published in these *Proceedings*² it was shown in detail how the frequencies of the nine normal modes described above may be evaluated and checked against the frequency shifts observed in the scattering of light by diamond when it is traversed by the λ 2536.5 radiations of the mercury arc. We shall content ourselves here with reproducing below as figure 1 a chart showing the nine frequencies and their respective degeneracies. The two modes of oscillation normal to the cubic planes have an identical frequency of 1088 cm^{-1} . They have accordingly been shown as a single frequency with a degeneracy of 6.

To complete the picture, we require to know how the three translatory movements of the 16-atom group manifest themselves in the vibration spectrum

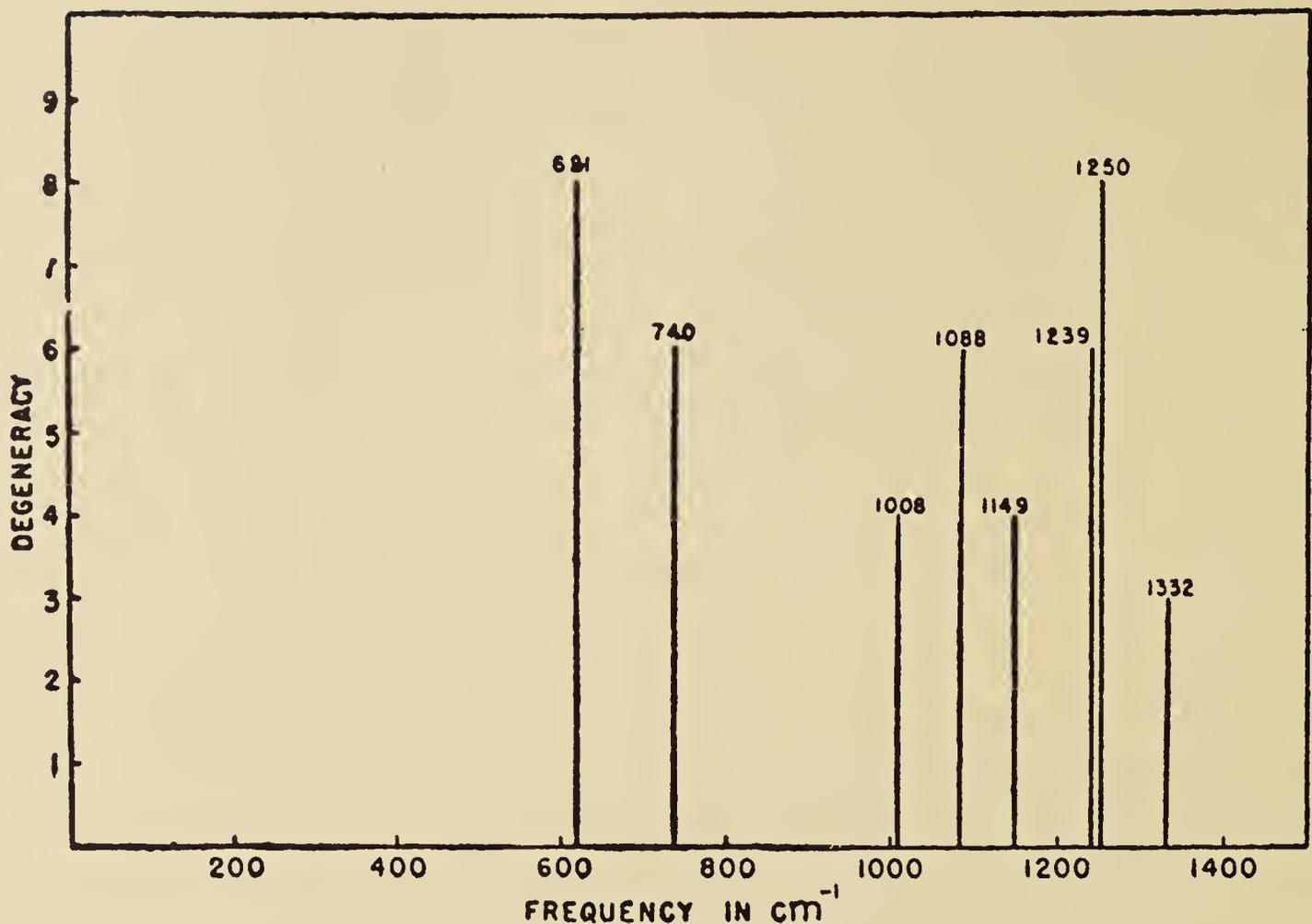


Figure 1. Chart of the vibration spectrum of diamond.

of the crystal. It is obvious that they would appear as internal vibrations in volume elements of larger size than the 16-atom group and therefore having lower frequencies. In dealing with vibrations of this nature, it is permissible to ignore the discrete atomic structure of the material. The larger the size of a volume element is, the lower would be the frequencies of its internal vibration. Considering volume elements of all possible sizes as the oscillators, their frequencies of internal vibration would evidently range from the lowest possible value $\nu = 0$ to an upper limit ν_L which may be taken equal to the lowest of the frequencies of vibration appearing in the chart (figure 1). The manner in which the disposable degrees of freedom of atomic movement are distributed over this range of frequencies is indicated by a simple argument. The number of volume elements of any specified dimension included in the crystal and hence also the number of degrees of freedom represented by their translations diminish in inverse proportion to the cube of the linear dimensions, while the frequencies of their internal vibration would vary inversely as the first power of the same. Hence the number of degrees of freedom appearing as internal vibrations of the volume elements and having frequencies between 0 and ν would be proportional to ν^3 . By differentiation, we obtain the result that the number of degrees of freedom appearing between frequencies ν and $\nu + d\nu$, in other words, the number of oscillators in the crystal having frequencies in that range would be proportional to $3\nu^2 d\nu$. The constant of proportionality may be deduced at once from the

consideration that on integration between zero and the upper limit ν_L , we should obtain as the total number of oscillators three times the number of 16-atom groups comprised in the crystal.

3. The heat capacity of diamond

Having thus ascertained the nature of the complete vibration spectrum of diamond, we proceed to make use of the theory of Einstein and obtain an expression for the heat content of the crystal as a function of the temperature. This appears as a sum of two quantities; the first is a summation of the average energies of the individual oscillators having the discrete frequencies shown in the chart (figure 1) multiplied by their respective degeneracies and by the total number of 16-atom groups contained in the crystal. The second part is a summation of the average energies of vibration of the oscillators of larger sizes having various frequencies from 0 to ν_L , and this takes the form of an integral between these limits of frequency. The details of the calculations have already been given in the earlier paper and it is therefore sufficient to reproduce the final results here in tabular form.

Table 1. Theoretical computation of the atomic heat of diamond
(Calories per gram-atom per degree)

Absolute tempe- rature	Discrete frequencies	Residual spectrum	Total	Absolute tempe- rature	Discrete frequencies	Residual spectrum	Total
15°	—	0.00014	0.00014	200	0.4069	0.1631	0.5700
20	—	0.00033	0.00033	225	0.5894	0.1895	0.7789
25	—	0.00064	0.00064	250	0.7844	0.2124	0.9968
30	—	0.0011	0.0011	275	1.0137	0.2319	1.2456
40	—	0.0026	0.0026	300	1.2418	0.2486	1.4904
50	—	0.0051	0.0051	350	1.700	0.275	1.975
60	—	0.0088	0.0088	400	2.139	0.294	2.433
70	0.0005	0.0140	0.0145	450	2.538	0.308	2.846
80	0.002	0.0207	0.0227	500	2.892	0.319	3.211
90	0.0056	0.0290	0.0346	600	3.469	0.334	3.803
100	0.0128	0.0388	0.0516	700	3.899	0.344	4.243
120	0.0419	0.0619	0.1038	800	4.2 4	0.350	4.574
140	0.0957	0.0877	0.1834	900	4.465	0.355	4.820
160	0.1758	0.114	0.2898	1000	4.653	0.358	5.011
175	0.2517	0.1333	0.3850	1100	4.797	0.360	5.157

It will be seen that the contribution from the set of discrete frequencies becomes negligible at temperatures below 60° Abs. At and below that temperature, the

residual spectrum of frequencies alone is responsible for the entire heat capacity of the crystal. At higher temperatures, however, the contribution of the spectrum of discrete frequencies rapidly increases and ultimately becomes responsible for all except 1/16th part of the specific heat.

In order to exhibit the over-all success of the theory in explaining the thermal behaviour of diamond, the figures for the atomic heat shown in table 1 have been plotted as a curve (figure 2) on a scale which is adequate to represent the data

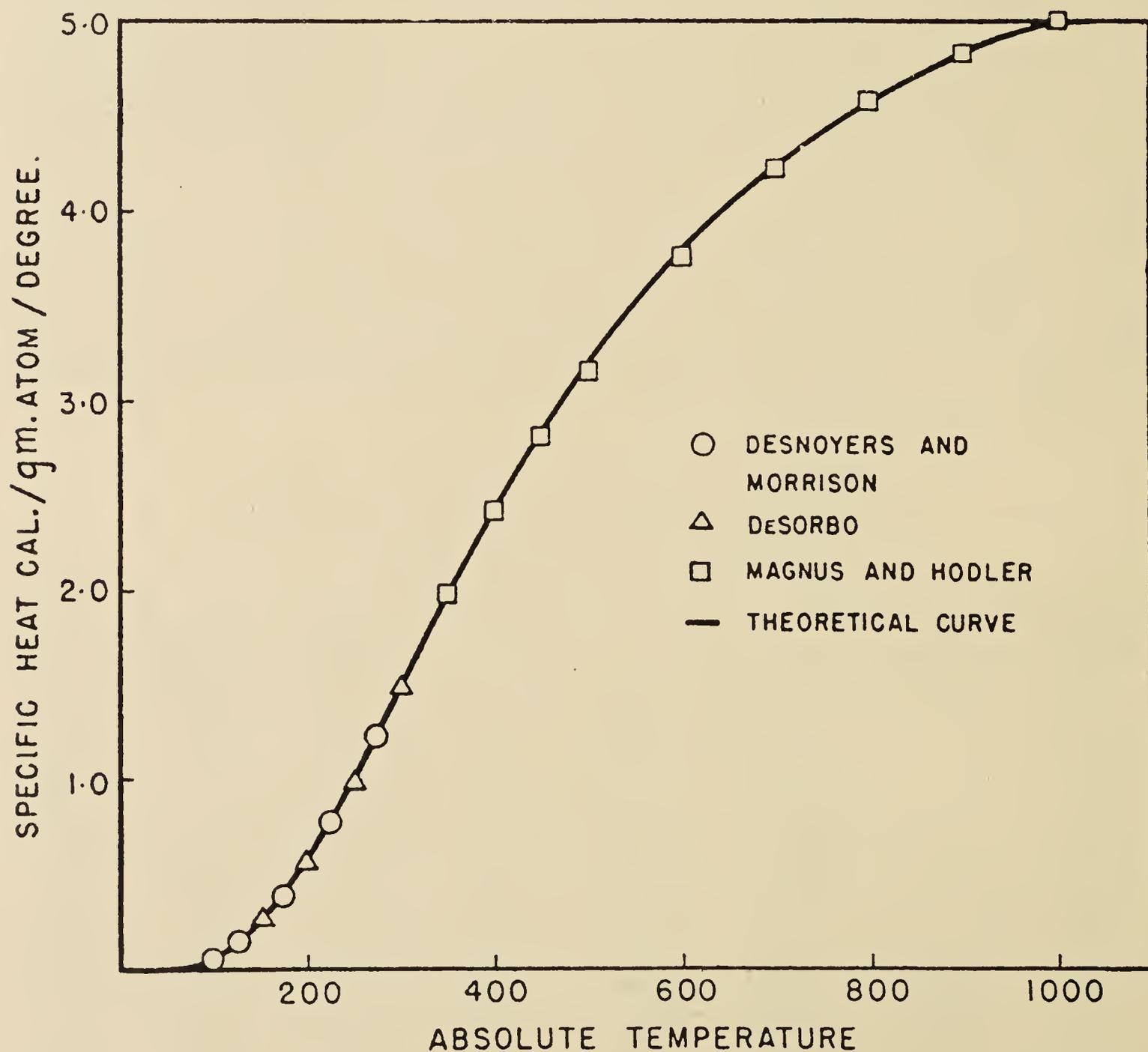


Figure 2. Specific heat of diamond from 0° to 1000°.

except in the region where it runs nearly parallel to the axis of temperature. In the temperature range between 300 and 1000° K, the values determined by Magnus and Hodler have been used, while in the lower ranges, the data of DeSorbo as well as those reported by Desnoyers and Morrison have been put in. It will be seen that no deviations between theory and experiment which are at all significant are noticeable on the scale of the graph.

For temperatures below 300° , the determinations by Pitzer, DeSorbo and by Desnoyers and Morrison are available, but since the two latter sets of determinations are in good agreement, they have been plotted in a graph covering the temperature range between 160 and 300° K (figure 3). The scale on which this

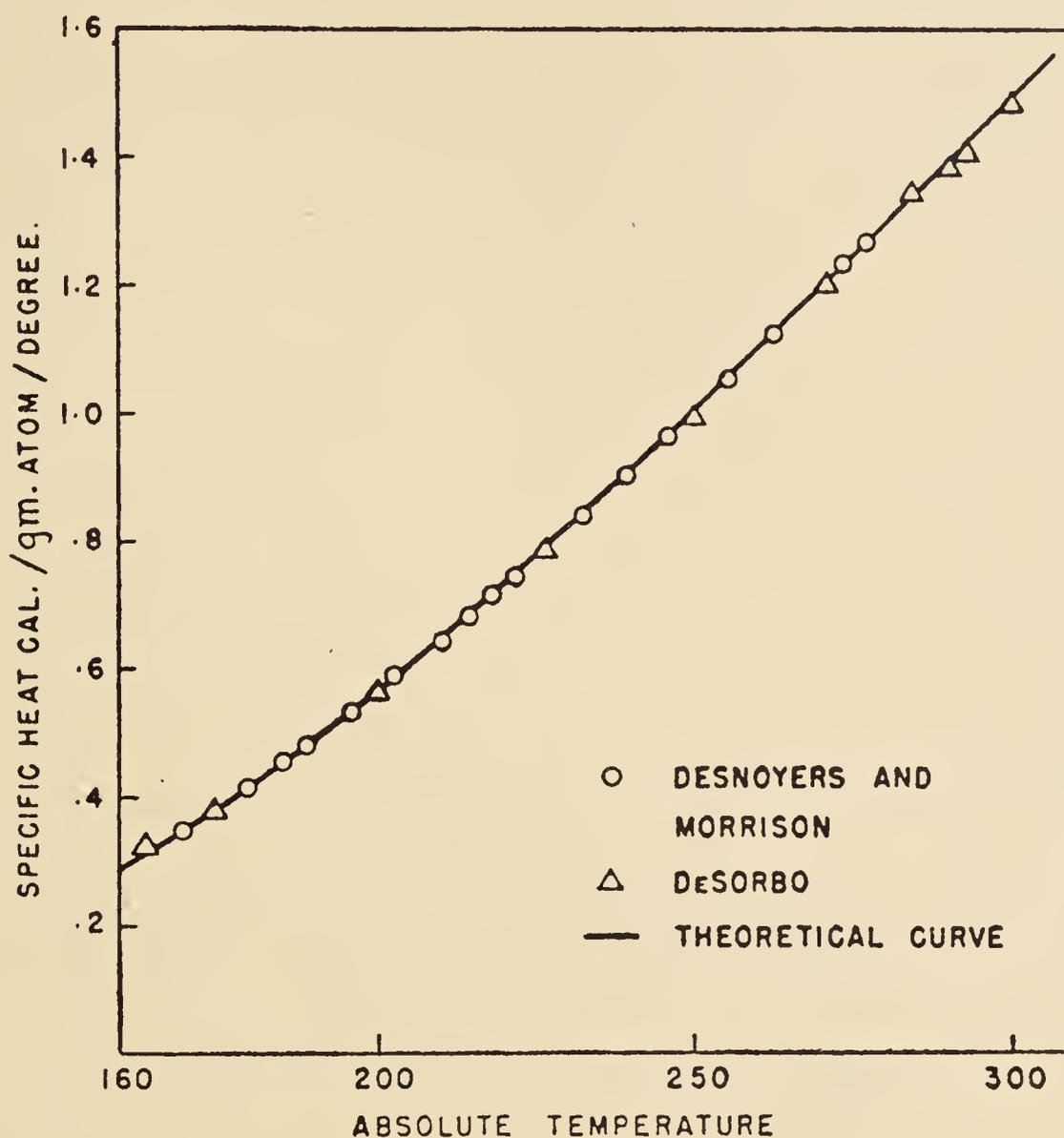


Figure 3. Specific heat of diamond from 160° to 300° .

figure has been drawn is adequate to disclose any systematic deviations between theory and experiment, had such existed. No such deviations are noticeable and hence it is evident that throughout the range of temperature in which the spectrum of discrete frequencies is principally responsible for the heat capacity of diamond (160 to 1000° K), the theory is in very satisfactory accord with the facts.

We shall next consider the very lowest temperatures where the value of C_p retreats into the third or fourth decimal place. The theoretical curve for this region has been drawn in figure 4, an adequately large scale being used for the ordinates, and the data reported by DeSorbo and by Desnoyers and Morrison have been plotted alongside of it. At the lowest temperatures the values of DeSorbo exhibit a distinct scatter, many of them lying above the theoretical curve. On the other hand, the more recent data of Desnoyers and Morrison lie

smoothly on the curve up to 50° . The agreement between theory and experiment in this range made apparent by the graph must be considered highly satisfactory.

In the temperature range between 50° and 60° K, the experimental values plotted in figure 4 lie above the theoretical curve, the magnitude of the differences being a few units in the fourth place of decimals. From figure 5 which represents a

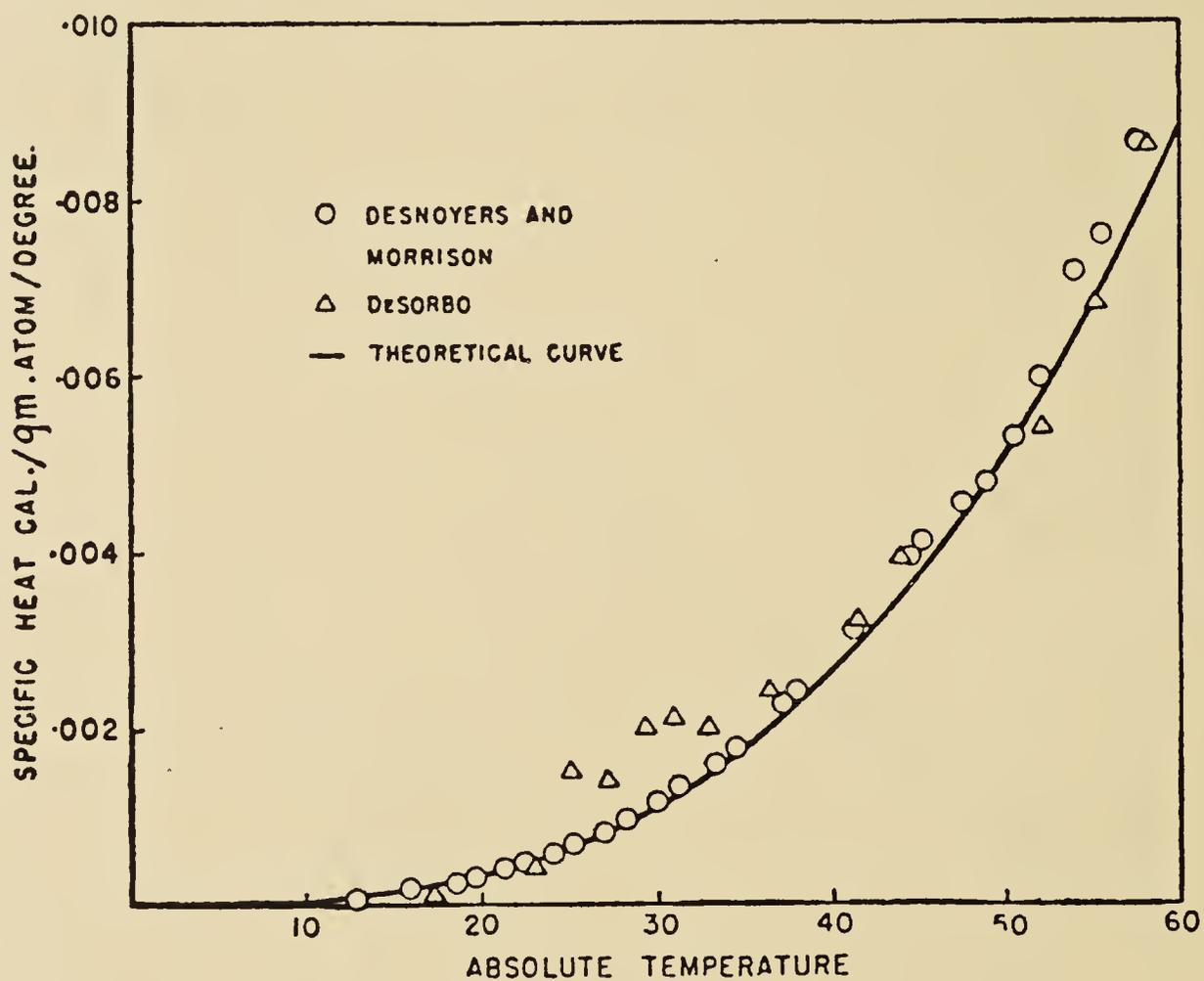


Figure 4. Specific heat of diamond from 0° to 60° .

comparison between theory and experiment in the range between 60° and 160° K it will be seen that such differences become distinctly more pronounced at higher temperatures, reaching a maximum value of 0.007 at about 100° ; they steadily diminish again at higher temperatures and finally cease to be noticeable on the graphs beyond 150° K. Since the value of the specific heat at 100° K is itself very low, being only 0.059, the difference between theory and experiment expressed as a percentage of the specific heat is 12%, but to express the difference in this way exaggerates its significance. Since, however, the discrepancy is real, we shall consider and comment upon its origin.

4. Spectroscopic behaviour of non-ideal diamonds

An explanation of the differences which are noticeable between theory and observation in the values of C_p in the range between 50 and 150° K is not far to

seek. The theoretical calculations refer to the case of an ideal crystal. They could therefore be expected to show a complete agreement with the experimentally determined specific heats if only the latter had also been made with ideal diamonds. Actually, however, determinations of specific heat require fairly large masses of material and it is therefore inevitable that they are made with diamonds of an inferior sort. It may be noted that DeSorbo used 80 grams of fragmented bort. He noticed that some of the crystals exhibited colour and also that about 20% of the material was fluorescent. Desnoyers and Morrison report that the sample used by them consisted approximately of 160 grams of industrial

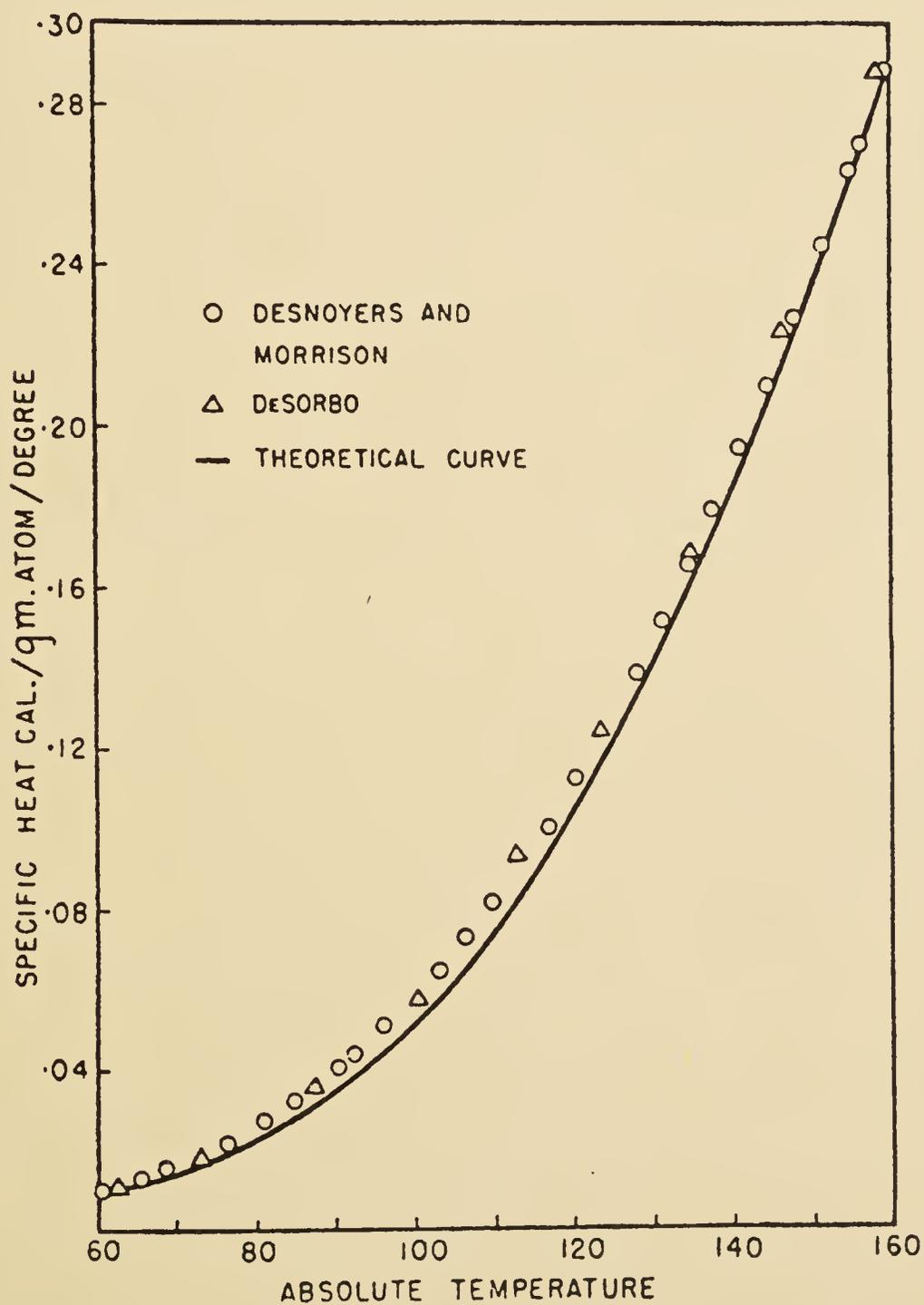


Figure 5. Specific heat of diamond from 60° to 160°.

diamonds, their average dimensions being about 3 mm. They also remark that most of their diamonds were lightly coloured, either yellow, brown or green but that none contained occlusions. It is evident from these descriptions that we are concerned here with the class of diamond that exhibits its non-ideality of crystal structure in a visible manner, in other words, shows colour in daylight and luminescence under ultra-violet illumination.

The spectroscopic behaviour of diamonds of all sorts has been investigated by a variety of methods over a period of many years by the author and his collaborators. It will suffice here to refer to the results reported in a paper by Miss Anna Mani³ recording a detailed study of the fluorescence and absorption spectra of twenty-two diamonds of various sorts. When the crystals are cooled down to liquid air temperature, these spectra sharpen notably, and it then becomes possible to analyse them in detail. Intercomparison of the fluorescence and absorption spectra enables the frequencies representing electronic transitions to be identified and distinguished from those due to the vibrational transitions appearing in combination with them. The result emerges clearly that the spectroscopic behaviour of diamonds which are colourless as seen by daylight and of those which exhibit various shades of brown, yellow or green is strikingly different. Diamonds of the former sort exhibit a blue fluorescence and the atomic vibration spectrum deduced from studies thereof is generally similar to that shown in the chart reproduced above as figure 1 in the text. On the other hand, diamonds exhibiting visible tints by daylight fluoresce with a greenish yellow colour, the analysis of the spectrum of which discloses many features both in the electronic and atomic vibration spectra which are absent in the blue luminescence of colourless diamonds. The most prominent of the additional features in the vibration spectrum is a band stretching from 257 to 443 cm^{-1} with its peak at 359 cm^{-1} .

It is clear from the facts recited above that the atomic vibration spectrum of non-ideal diamonds differs notably from that of the ideal material. The difference arises chiefly in the region of the residual spectrum of frequencies and may be described as an enhancement of its strength in the region of frequencies about 359 cm^{-1} . Since the total number of atomic degrees of freedom is invariant, such enhancement would necessarily involve a diminution in the strength of the residual spectrum at higher frequencies between 359 cm^{-1} and the upper limit of 621 cm^{-1} . A change in the character of the residual spectrum of the nature indicated would evidently result in altering the specific heat of the crystal. The Einstein function for a frequency of 359 cm^{-1} has a negligible value at temperature below 50° K . It increases most rapidly in the temperature range in the vicinity of 100° , and at higher temperatures tends more slowly towards its limiting value. The change in the character of the residual spectrum would thus result in an increase of the specific heat of non-ideal diamonds which would be vanishingly small at very low and at very high temperatures and would be most prominent at about 100° K . This describes what is actually observed.

Acknowledgement

The author much appreciates the courtesy of Messrs Desnoyers and Morrison in having made the results of their valuable new determinations available to him in advance of publication.

Summary

The evaluation of the heat capacity of diamond on the basis of the theory of specific heats advanced by the author is discussed and the results are compared graphically with the latest available experimental data. A striking over-all agreement emerges over the whole of the temperature range between 0° to 1000° K. The experimental values are however slightly in excess of the theoretical ones in the limited range between 50° and 150° K, the difference in the value of C_p being a maximum of 0.007 at about 100° K and ceasing to be noticeable both below 50° K and above 150° K. This small excess is explained as a consequence of the use in the experimental determinations of industrial diamonds whose spectroscopic behaviour is observably different from that of the ideal material.

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The diffraction of X-rays by diamond—Part I

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1. Introduction

By reason of its remarkable physical properties, diamond stands out uniquely as the crystal which shows us the way to a correct understanding of the fundamental aspects of the physics of the solid state. The atomic vibrations in crystals, the theory of their specific heats and their spectroscopic behaviour may be mentioned in this connection. These topics formed the subject of recent memoirs published in these *Proceedings*, and the experimental results obtained with diamond figured very prominently in them. The present communication deals with the X-ray diffraction effects exhibited by diamond and considers them from both the theoretical and experimental standpoints. It emerges that diamond has a great deal to teach us regarding the fundamental aspects of the subject of X-ray crystallography and indeed compels us to approach the subject from new points of view.

The present investigation stems from a report from the author's laboratory published in the year 1940 under the title "A new X-ray effect" (*Curr. Sci.*, 1940, 9, 165–67). That report recorded the discovery of the very striking and indeed surprising features which reveal themselves in strongly exposed X-ray diffraction patterns of diamond. It was very clear that the phenomena stood outside the framework of the classical theory of X-ray diffraction. It was accordingly suggested that they had their origin in the quantum-mechanical excitation of the atomic vibrations in diamond by the monochromatic X-ray beam traversing it, the X-rays being themselves reflected as a result of such excitation with a change of frequency. It was explained in the report why it was possible for reflections of this nature to be observed even when the setting of the crystal was different from that ordinarily required for a reflection of the X-rays by the same lattice planes.

The instrumental equipment available for the research at that time was, unfortunately, not of sufficient power to enable the subject to be explored with any degree of completeness. The investigation had accordingly to be laid aside and the circumstances in which the author found himself did not, for many years, permit of its being resumed. Happily, however, it has now been possible to take up the work once again, not only with new and more powerful instrumental aid,

but also with fresh theoretical ideas derived from the work of the author in the related fields referred to earlier in this introduction. The results are now laid before the reader.

Part I of the paper considers the theory of X-ray diffraction by crystals in general from a fundamentally new standpoint. Part II considers the application of the theory to the particular case of diamond. Part III presents the results of a detailed experimental investigation of the case.

2. The structure of crystals

The conventional view of a crystal as an assembly of atoms arranged in a regular three-dimensional array in space is neither useful nor enlightening when we seek to obtain an insight into the behaviour of crystals when traversed by radiation in the different ranges of frequency. It is necessary indeed to lay aside that view and regard a crystal as a system composed of two kinds of charged particles, namely the nuclei and the electrons, their relative numbers being determined by the magnitudes of their charges. Diamond, for example, is an assembly of carbon nuclei and of electrons, the latter being six times as numerous as the former.

The atomic nuclei have enormously larger masses than the electrons and it is this circumstance that determines the manner in which the two sets of particles arrange themselves in space. According to the fundamental notions of the quantum theory, it is not meaningful to regard the electrons as located at any specifiable points in space, while on the other hand, it is permissible to do so in respect of the nuclei. The Coulomb forces exerted by the nuclei on the electrons tend to draw the latter together and hold them in dynamic equilibrium. Accordingly, what may be described as a cloud of negative charge gathers round each nucleus. But when we raise the question as to what determines the position of the nuclei in space, the answer, remarkably enough, is to be found in these very clouds of negative charge which each nucleus gathers around itself. Indeed, it is the electrons which determine the location and ordering in space of the nuclei. Accordingly, it would be appropriate to describe a crystal as consisting of two distinct assemblies, namely an assembly of nuclei whose positions it is possible to specify with some measure of precision, and an assembly of electrons. It is the interaction of these two assemblies with each other that determines the architecture of the crystal and its physical behaviour. This view of crystal structure will be found most illuminating when we proceed to consider the phenomena resulting from the passage of radiation through the crystal.

3. The response of crystals to radiation

The tremendous disparity in the masses of the nuclei and of the electrons justifies us in ignoring any movement of the atomic nuclei which results directly from the

action of the electric field of the radiation on the charges carried by the nuclei. What we need consider in every case is the effect of the radiation field on the electronic clouds. But since these are held in place by their interactions with the atomic nuclei, the latter would also tend to be disturbed when the electronic clouds are set in motion by the field. These considerations are valid irrespective of the individual features of the crystal structure and of the frequency or wavelength of the incident radiation. But since the response of the electrons to the field of the incident radiation would depend on these latter factors, the nature and extent of the movements of the atomic nuclei consequent thereon would also be influenced by those factors.

We may illustrate the foregoing remarks by considering first the cases in which the frequency of radiation lies in the infra-red range. Viewing the matter classically, the effect of the radiation on the electronic clouds in this case would be to produce periodic displacements to and fro of the electronic clouds with the same frequency. These displacements would, however, be limited by the binding of the electrons to the nuclei. Even when the frequency of the incident radiation coincides with a natural frequency of vibration of the atomic nuclei about their positions of equilibrium, it would not necessarily follow that such vibration is excited by the field. Indeed, it is well known that in many cases, the field does not excite the vibrations; in other words, the vibrations are not active in the absorption of the infra-red radiation. In order that any given mode of vibration should be excited by the incident radiation field and thereby rendered infra-red active, it is necessary that a certain lack of symmetry in the structure of the crystal or of the particular mode of vibration results in the movements of the nuclei being accompanied by a periodic displacement to and fro of the electronic clouds which hold the nuclei together. The selection rules which define the conditions under which any particular mode of vibration is active in the absorption of infra-red radiation are, indeed, based on considerations of this nature. That they are in agreement with experience demonstrates the validity of the present approach to the subject.

Coming now to the case of visible light, the response of the crystal to the field of the incident radiation would be determined by the relation between the frequencies of the incident radiation and the characteristic frequencies of vibration of the electronic clouds. Further, since the frequency of the radiation is much higher than the natural frequencies of vibration of the nuclei, the possibility of the incident radiation exciting the latter in the manner considered in the preceding paragraph would not arise at all. There are however possibilities of the nuclear vibration being excited by the electronic movements in a different way. Considering those electrons which hold together the different nuclei and thus form part of the architecture of the crystal, it is evident that any approach or recession of such nuclei from each other would influence the characteristic frequencies of the electronic clouds attached to them. This is equivalent to stating that the response of the electronic clouds to the field of the incident light would be

modified or modulated by the natural frequencies of the nuclear vibrations. That such an effect actually arises is demonstrated by the fact that when monochromatic light traverses a crystal, and the light diffused in its interior is spectroscopically examined, monochromatic radiations are observed in it whose frequencies differ from that of incident light by amounts equal to the characteristic infra-red vibration frequencies. Whether or not any particular mode of vibration of the nuclei thus reveals itself is determined by the circumstances of the case. The selection rules which express these circumstances are naturally different from those that determine the activity in infra-red absorption.

The frequency of X-radiation is very much higher than that of either visible light or of infra-red waves, and the phenomena arising from their passage through crystals would naturally be determined by the high frequencies and correspondingly short wavelengths of the rays. We have, in the first instance, to consider the effect of the radiation field on the electronic clouds. But it is not possible to ignore the fact that the electronic clouds are held in their places by the atomic nuclei and that, consequently, not only the electronic clouds but also the atomic nuclei would tend to be disturbed by the X-radiation. There is every reason therefore to expect that the effects arising from such disturbance of the nuclei would manifest themselves in the X-ray diffraction patterns of the crystal.

The foregoing represents the general point of view which will be developed and discussed in greater detail in the present series of papers. Its consequences will also be compared with the facts of observation. We shall find that it receives the clearest possible support in the phenomena exhibited by diamond in its X-ray diffraction patterns.

4. X-rays and crystals

The observational basis of X-ray crystallography is the selective reflection of X-rays by the atomic layers in a crystal at angles of incidence determined by the wavelength of X-rays and the spacing of the layers. The phenomena is clearly analogous to the familiar effect of iridescence exhibited by regularly stratified media on which visible light is incident. Hence it is quite natural to explain the phenomena of X-ray diffraction by crystals on similar lines. We assume the crystal to be a material of which the optical polarisability for X-ray frequencies exhibits space-periodic variations in three dimensions. A determination of the settings of the crystal at which the X-ray reflections for a known wavelength are observed enables us to determine the spacings of the stratifications in various directions as also their relative orientations. A comparative study of the intensities of the various reflections enables us to go further and obtain a measure of the magnitude of the periodic variations of the polarisability for X-ray frequencies appearing in each set of stratifications. The entire procedure is phenomenological in character. In endeavouring to deduce from the experi-

mental results a picture of the ultimate structure of the crystal, various difficulties arise which we shall not discuss here. What we are actually concerned with is the meaning of the phrase “polarisability for X-ray frequencies” employed above in terms of the ultimate structure of the crystal.

In classical optics, where we are concerned with the behaviour of media which can be regarded as continuous, the term polarisability has a simple and definable meaning, namely, the strength of the electric dipole per unit of volume induced by an external electric field of unit strength. Difficulties arise when we endeavour to take over this description into the region of high frequencies and short wavelengths. These difficulties are of two kinds. Firstly, the medium can no longer be regarded as a continuous and structureless substance, since it actually consists of a set of discrete particles arranged in layers. The second difficulty is that these particles are not all similar and similarly circumstanced. In particular, the nuclei and the electrons have very different masses and are oppositely charged; the interactions between them enter fundamentally into the problem of determining the response of the medium to the field of the incident radiation.

A way of escape from the difficulties indicated above may be sought for by regarding the recognisable units in the structure as “diffracting particles” in the sense of classical optics. We find however that such a procedure is not sustainable. For example, the individual electrons in the crystal cannot be assigned the role of “diffracting units”. For, as already remarked, an electron does not possess any precisely definable location in space and hence the phase of any radiation that it could diffract would be indeterminate. An even more fundamental difficulty is that if an individual electron does interact with X-rays, the result is a secondary radiation of altered wavelength, in other words the Compton type of scattering. The alternative approach of regarding the individual *atoms* in the crystal as the “diffracting units” is also not sustainable. For, in any actual crystal, the atoms are held in their places by the electrons which link them together and these electrons cannot therefore be regarded as the exclusive possession of any particular atom. Taking for instance the case of diamond, only two out of every six electrons can with any measure of justification be considered as attached to an individual carbon nucleus. The remaining four electrons enter into the architecture of the crystal and hence must be considered as held in common with other atoms.

In view of the situation stated above, it is clear that the only logically sustainable approach to the subject of X-ray diffraction is that which proceeds on the following basis: *the X-ray reflections by a crystal are a co-operative effort of the entire structure, meaning thereby all the nuclei and all the electrons included in it.*

5. The energy levels of crystals

The present approach to X-ray diffraction problems differs from that customarily adopted in two respects. In the first place we recognize that the atomic nuclei have

a part to play in the phenomena since on the one hand, they hold the electrons in place and on the other hand are themselves held in place by the electrons. Further, what we shall actually concern ourselves with is not the behaviour of the individual electrons or of the individual atoms in the crystal, but the behaviour of the two assemblies consisting of nuclei and of electrons respectively constituting the crystal when it is traversed by the X-radiation. This approach brings the phenomena of X-ray diffraction into the closest relationship with the behaviour of crystals when traversed by ultra-violet, visible or infra-red radiation. In all such cases we are concerned with the changes in the energy levels of a crystal which are or could be induced by the radiations traversing it. As we have two sets of particles which differ greatly in their masses, the possible changes in the energy levels are of two kinds which in the usual language of spectroscopy may be described as changes in the electronic levels and the vibrational levels respectively. The simplest cases are those in which there is no change in either the electronic or vibrational energy states of the crystal when traversed by radiation. This would correspond to a simple undisturbed transmission of the radiation through the crystal in the case of visible or ultra-violet light. In the case of X-radiation, however, the stratifications of optical polarisability in the structure of the crystal can in appropriate circumstances result in geometric reflections of X-rays in various directions. In the language of the quantum theory, such reflections would be described as the result of an exchange of momentum without an exchange of energy between the radiation and the crystal. Still another possibility has to be recognised, namely, that while the initial and final *electronic* energy states are the same, the radiation induces a change in the *vibrational* energy level which persists. When and in what circumstances such a process can occur as the result of the passage of X-radiation, and what would be the observable results of such a process are the questions which we shall proceed to consider.

The answers to the questions raised above emerge when we consider the effects observed respectively when a crystal is traversed by radiation in the infra-red and in the visible regions of the spectrum. In the former case we are concerned with an actual absorption of the radiation. In the latter case we have a simple transmission accompanied by a diffusion or scattering with shifts of frequency indicating that changes in the vibrational energy levels have been induced by the incident light. It should not be imagined that each and every characteristic mode of vibration can manifest itself in the infra-red absorption spectrum and in the scattering of light as a frequency shift. This is very far indeed from being the case. Whether a particular mode of vibration does or does not so manifest itself is determined by certain selection rules which are different for infra-red absorption and for light-scattering. Why this is so becomes clear when the mechanisms respectively of infra-red absorption and of the scattering of light with change of frequency are examined. The latter effect is explained as arising from the variations of the optical polarisability of the crystal for visible light which accompany changes in its infra-red energy levels. On the other hand, infra-red

absorption arises from the displacements of electric charge produced by the incident radiation. The question arises whether effects of the same nature can be induced by X-radiation. It is obvious that any change in the optical polarisability for X-rays produced by the changes in the infra-red energy levels of the crystal would, in view of the very high frequencies of X-radiation, be entirely negligible. On the other hand, the periodic displacements of electric charge associated with vibrational transitions which are active as absorbers of infra-red radiation necessarily involve periodic displacements of the stratifications of optical polarisability which give us the X-ray reflections by the crystal. *It follows that when X-radiations traverse a crystal, they can induce changes in its vibrational energy levels, provided that such changes involve displacements of electric charge—in other words, provided that the modes of vibration under reference are active as absorbers of infra-red radiation.*

6. X-ray reflection with change of frequency

We have now to consider what would be the consequence of a change in the vibrational energy levels of crystals induced by X-rays in the circumstances stated above. The question arises whether the observable result of such a process would be a diffusion of the X-rays in various directions or else a reflection similar to that ordinarily observed involving no exchange of energy. Before this can be answered, we have to ask ourselves: What is the nature of the vibration spectrum of a crystal? This question has already dealt with by the author in various recent publications and the same ground need not therefore be traversed here once again. As has been shown in the publications referred to, theory and experiment alike indicate that the vibration spectrum of a crystal containing p atomic nuclei in each unit cell consists of a set of $(24p - 3)$ monochromatic frequencies, accompanied by a residue representing the three omitted degrees of freedom which constitutes a continuous spectrum of low frequencies. Amongst the $(24p - 3)$ modes, in $(3p - 3)$ modes which are the only ones with which we are concerned in the present paper, the vibration repeats itself with identical frequency and amplitudes and phases in the successive cells of the crystal structure. It follows from this that the changes in the corresponding vibrational levels induced by the incident X-radiation would extend over the entire volume of the crystal traversed by the incident X-ray beam. As a consequence of this again, the X-rays would be regularly reflected by the stratifications of the crystal; such reflection involves a transfer of energy between the radiation and the crystal equal to the vibrational frequency multiplied by Planck's constant. *Hence, the frequency of the reflected X-rays would differ from that of the incident X-ray beam by the frequency of the vibrational mode excited.* As has been explained in the preceding section, such a process is only possible in respect of the modes of vibrational which are active in the absorption of infra-red radiation.

The result stated above has a classical analogue in the reflection of light by a stratified medium which is assumed to execute oscillations of small amplitude normal to its layers. (An oscillation parallel to the layers would obviously be without effect.) It can readily be shown that the reflected wave of the original frequency $A \sin 2\pi\nu t$ would be accompanied by *two* additional components which are respectively of diminished and increased frequency,

viz.,

$$\pi \cdot A \cdot d^*/d \cdot \sin 2\pi(\nu + \nu^*)t,$$

and

$$\pi \cdot A \cdot d^*/d \cdot \sin 2\pi(\nu - \nu^*)t,$$

where d and d^* are respectively the spacing of the stratifications and the amplitude of their oscillation, while ν and ν^* are respectively the frequencies of the incident radiation and of the oscillation of the stratifications. The equality of amplitude of the reflected waves of enhanced and diminished frequency is a natural consequence of our assuming the oscillations of the layers to subsist of themselves. In the quantum theory, on the other hand, the oscillations are *induced* by the incident radiation, and hence the two components would, in general, be of very different intensities; their ratio is determined by thermodynamic considerations and is expressible in terms of the Boltzmann factor $\exp(-h\nu^*/kT)$.

The classical analogy referred to above leads to some general inferences regarding the intensity of the X-ray reflections with altered frequency in relation to the intensity of the X-ray reflections of unmodified frequency given by the same set of lattice planes. We notice in the first place that the two are proportional to each other. Hence, if one is absent, the other would also be absent. In other words, the so-called missing reflections familiar to the X-ray crystallographer would also fail to manifest themselves as dynamic reflections. Further, we could normally expect to observe the latter only as accompaniments of the stronger reflections of the ordinary kind. Their relative intensity is determined by the square of the ratio d^*/d , where d^* is the amplitude of oscillation of the stratifications and d is their spacing. Since d^* is a measure of the displacement of electric charge which is responsible for the activity of the mode in the absorption of infra-red radiation, it follows, firstly, that inactive modes would not give rise to dynamic X-ray reflections, and secondly, that the greater the infra-red activity of a mode, the more intense would be the dynamic X-ray reflections associated with it.

7. The phase-waves of dynamic reflection

The possibility of X-radiation exciting one of the $(3p - 3)$ characteristic modes of nuclear vibration and being itself reflected in the process was deduced above on the assumption that the wavelength of the X-rays, the spacing of the stratifications, and the angle of incidence on them are related to each other in the same

manner as that necessary for a reflection of the ordinary kind. In these circumstances, the excited vibration necessarily repeats itself with the same frequency and also with the same amplitudes and phases in every cell of the structure traversed by the X-rays.

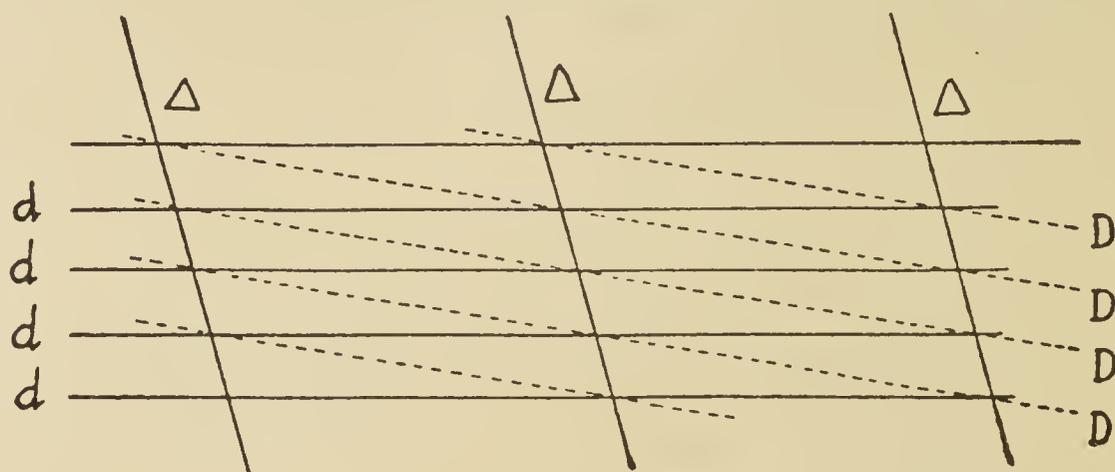


Figure 1

For X-ray reflections with a change of frequency to be observable at other settings of the crystal, it is necessary that the vibrations excited are everywhere similar, but that the phase of the excited vibration in the individual cells of the structure alters progressively through the crystal in such a manner that the vibrations excited in all the irradiated cells conspire to give a coherent reflection. The condition for this to be possible is most readily stated in the form of a diagram (figure 1 in the text). The lines marked $d d d$ represent the traces on the plane of the paper of the stratifications in the crystal. The planes marked $\Delta \Delta \Delta$ similarly represent the traces on the plane of the paper of the *phase-waves*, in other words of the planes along which the internal vibrations of the crystal have identical phases. It is evident from the figure that the planes marked $D D D$ cutting across both of them would represent the stratifications which play the same role for the dynamic reflections that $d d d$ play for the static ones. The relationship between the spacings D , d and Δ is given by the vectorial formula

$$\frac{\vec{1}}{D} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta}. \quad (1)$$

It needs to be explained why the situation indicated in figure 1 can arise consistently with the principles of dynamics and of the quantum theory. A vibration in which the frequency as well as the amplitudes and the phases are the same in every cell of the crystal structure is the only possible vibration having the characters of a normal mode. Since, however, the interatomic forces in crystals are essentially short-range forces, it is permissible to regard a crystal as made up of a great number of quasi-independent oscillators which have common modes and frequencies of vibration. Indeed, this is the approach which has necessarily to be adopted in developing the theory of the specific heats of crystals. It leaves

out of account the small uncertainties in the frequency of vibration incidental to a limitation in size of the individual oscillators. In our present problem, therefore, it is permissible to consider modes of internal vibration which are the same everywhere in the crystal but in which the phase of vibration in the individual cells alters progressively as we move through the crystal. If Δ is large enough compared with d , the vibration would be practically indistinguishable from the limiting case in which Δ is infinite. But as Δ is diminished, what we have in the crystal is not a normal mode but a *forced* oscillation of which the frequency is different, the more so, the smaller Δ is. In other words, a dynamic reflection in these circumstances results from a forced oscillation excited by the X-rays with a frequency differing slightly from that of the free oscillations of the structure. Hence, using the language of the quantum theory, we may infer that the probability of such an event happening would diminish rapidly as Δ becomes smaller. In consequence, we would find that the dynamic reflection has the maximum intensity when the setting of the crystal is that at which the ordinary reflections also appear; the intensity would fall off rapidly as the crystal is moved away from that setting in either direction.

8. The geometric law of dynamic reflection

The construction shown in figure 1 enables us to deduce some general results regarding the geometric behaviour of the dynamic reflections. If the phase wavelength Δ is infinite, the dynamic stratifications $D D D$ would coincide with the static layers $d d d$. Hence, if the X-rays are incident on the latter at the correct angle for a regular reflection of the ordinary kind, the dynamic reflection would also appear in the same direction superposed on it. In the general case, the direction in which the reflection would appear would be determined by the orientation and the magnitude of the phase-vector. If both of these quantities can vary arbitrarily, then nothing in the nature of a regular reflection would be possible. If, however, the orientation of the phase-vector is precisely defined, a monochromatic X-ray beam incident at a precisely defined angle on the lattice planes of a crystal can result in a dynamic reflection also appearing in a precisely defined direction; but unlike the static reflection in similar circumstances, it would be observable over a wide range of settings of the crystal. The plane of reflection would naturally be the plane of incidence of the X-rays on the dynamic stratifications and the angles of incidence and of reflection with respect to them would also be equal.

Figure 2 exhibits the geometric laws of dynamic reflection of X-rays in a readily comprehensible fashion. The directions of the vectors $\vec{1/d}$, $\vec{1/D}$, $\vec{1/\Delta}$ are represented by points on the surface of a sphere, the X-ray beam being assumed to traverse the crystal along the polar axis of the sphere. Three meridional circles have been drawn on the sphere passing respectively through those three points.

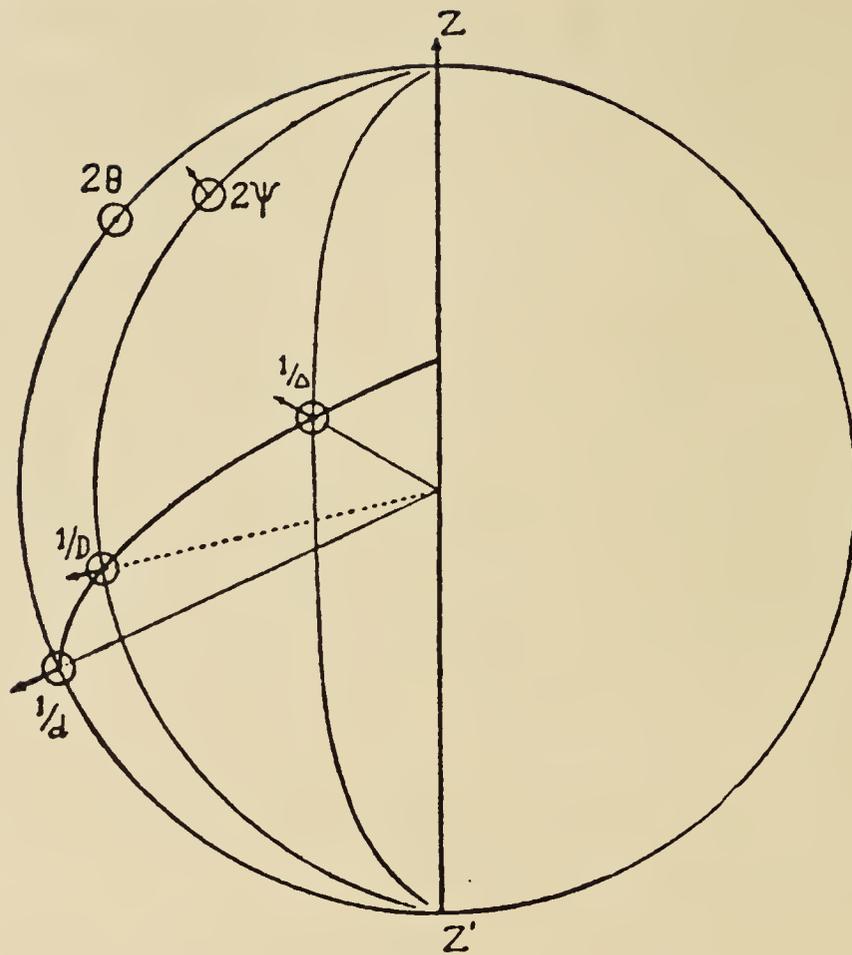


Figure 2

The first circle is evidently the plane of incidence of the X-rays on the lattice layers whose spacing is d . The second is the plane of incidence of the X-rays on the dynamic stratifications. The third circle is the plane containing the incident X-rays and the normal to the phase-waves. From equation (1) connecting the three vectors $\vec{1/d}$, $\vec{1/D}$ and $\vec{1/\Delta}$, it follows that the point representing $\vec{1/D}$ on our sphere would lie on a great circle drawn through $\vec{1/d}$ and $\vec{1/\Delta}$, its actual position on that circle being determined by the relative values of d and Δ . If θ be the glancing angle of incidence of the X-rays on the lattice layers of the crystal, a reflection would appear in a direction making an angle 2θ with the polar axis of the sphere on the first meridional circle, provided the condition $2d \sin \theta = \lambda$ is satisfied. This would correspond to the case in which the phase wavelength Δ is infinite. In the actual case to which the figure refers, the dynamic reflection would appear in a direction making an angle 2ψ with the polar axis of the sphere, ψ being the glancing angle of the incident X-rays on the dynamic stratifications. It is here assumed that the condition $2D \sin \psi = \lambda$ is satisfied. The figure indicates that the dynamic reflection deviates from the direction in which it would appear for an infinite phase wavelength, both along the meridional circle and transverse to it, to extents determined by the angle between the first and the third meridional circles as also by the angle of incidence of the X-rays on the lattice planes under consideration.

9. Summary

The theory of X-ray diffraction in crystals is discussed and it is shown that the X-ray reflections must be regarded as a co-operative effort of the entire structure in which the nuclei as well as the electrons play their respective roles. It is further shown that the passage of X-rays through a crystal and their reflection by the stratifications of electron density can simultaneously result in vibrational energy transitions, provided that the modes of vibration thus excited involve displacements of electric charge and are therefore active as absorbers of infra-red radiation. Vibrational modes of this kind when excited result in periodic displacements of the stratifications of electron density. Consequently, reflections appear whose frequencies are less (or greater, as the case may be) than the frequency of the incident X-radiation. It is explained why it is possible for such reflections to appear even when the setting of the crystal is different from that required for the usual or unmodified reflections. The geometry of the X-ray reflections which then appear in displaced positions is also discussed.

The diffraction of X-rays by diamond—Part II

SIR C V RAMAN

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1. Introduction

For various reasons, diamond is the ideal case for a consideration of the consequences following from the ideas set out in part I of this series of papers regarding the diffraction of X-rays by crystals. Since diamond is a cubic crystal of relatively simple structure, it is possible to determine and describe in purely geometrical terms the modes of vibration of which that structure is capable and with which we are concerned. It can also be shown that these modes have a high frequency, from which again it follows that they would not be thermally excited to any appreciable extent at ordinary temperatures. For the same reason also, it is permissible to ignore the disturbing effects, on the phenomena with which we are concerned, of the thermal agitation in the crystal. It accordingly becomes possible to present a very clear picture of the effects which may be expected to present themselves to observation in strongly exposed X-ray diffraction patterns of diamond, on the basis of the theory developed in part I.

2. The structure of diamond

Diamond exhibits in its structure a complete justification of Van't Hoff's hypothesis of the tetrahedral carbon atom. That hypothesis was originally put forward on the basis of the known chemical behaviour of carbon. It implies that the four valences which carbon exhibits in its compounds are tetrahedrally disposed in space and are indistinguishable from each other. Why this is so is one of the fundamental problems of theoretical chemistry. According to the spectroscopist's view of atomic structure, the nucleus of the carbon atom is surrounded by six electrons, two of which are in the inner or K-shell and the other four in the outer or L-shell. The latter four electrons again are assigned to two sub-groups, each containing two electrons. In the first sub-group, the electrons are assumed to be in the $2s$ state, while the two electrons in the other sub-group are in the $2p$ state. This situation of the four outer electrons is not in agreement

with that indicated by the facts of chemistry and hence it becomes necessary to modify the description of their states to bring it into line with the known chemical behaviour of carbon. All the four electrons have indeed to be considered as being in states indistinguishable from each other and so orientated that the resulting structure has perfect tetrahedral symmetry. Such a concept is necessary also to fit the picture of the carbon atom into the known facts concerning the structure of diamond. Having only two atoms in each unit cell, diamond nevertheless exhibits cubic symmetry. This situation requires that the nuclei of the carbon atoms occupy certain special positions in the crystal structure, namely, the points at which the four trigonal axes of cubic symmetry intersect each other.

The theory of hybridised orbitals is one of the best-known attempts in the direction of describing the electronic state of the carbon atom in such manner as to bring it into line with the hypothesis of Van't Hoff. As full accounts of that theory are to be found in several recent treatises, it is not necessary here to expound it in detail. It is sufficient to mention that the states of the four electrons are assumed in that theory to be representable as a superposition of four hydrogen-like wave-functions which are so chosen that all the four electrons appear in similar states differing only in their orientations, which again exhibit tetrahedral symmetry. In the wave-functions assumed for the purpose, the $2p$ states preponderate, and hence each of the four electrons is implicitly assumed to possess an orbital angular momentum about an axis which coincides in direction with its directed valence. We may remark that for the shell of valence electrons thus constituted to possess true tetrahedral symmetry, it is necessary that the orbital movements of the four electrons about their respective axes should be described in the same sense, that is to say, either all of them in a right-handed sense, or else all of them in a left-handed sense. We are thus led to recognize that there are two possible descriptions of the carbon atom, namely, a dextro-carbon atom and a laevo-carbon atom, which correspond respectively to the two possible senses of the orbital angular momentum of the electrons about the tetrahedral valence directions.

The considerations set forth above have important consequences in relation to the structure and physical properties of diamond. That crystal is usually described as made up of two non-equivalent sets of carbon atoms each located at the points of a face-centred cubic lattice; the two lattices interpenetrate each other in such manner that every carbon atom in one lattice is tetrahedrally surrounded by four others belonging to the other lattice. Accepting this description, it follows that in a truly homogeneous crystal of diamond, only one out of four possible situations can exist: (i) both lattices are occupied by dextro-carbon atoms, (ii) both lattices are occupied by laevo-carbon atoms, (iii) one lattice is occupied by dextro-carbon atoms and the other by laevo-carbon atoms, or (iv) the first lattice is occupied by laevo- and the second by dextro-carbon atoms. It is entirely possible that two or three or all four of these possible structures may exist simultaneously in different parts of the same crystal. It is sufficient, however, to consider here only

the case of truly homogeneous diamonds the structure of which is exclusively one or another of the four categories set out above.

3. The vibration spectrum of diamond

The vibration spectrum of a crystal containing p atomic nuclei in each unit cell consists of $(24p - 3)$ distinct modes with monochromatic frequencies, supplemented by a continuous spectrum which is the residue representing the three omitted degrees of translatory freedom of motion. Since the unit cell of diamond contains 2 atomic nuclei only, we have 45 possible modes of vibration with monochromatic frequencies. The description of these modes and the evaluation of their frequencies have been very fully set out in an earlier memoir published in these *Proceedings*. In two other memoirs again, it has been shown that the heat capacity of diamond over the entire range of temperatures may be quantitatively evaluated in terms of these frequencies. It is therefore unnecessary to traverse the same field again, and indeed in the present paper we are only concerned with the three modes of vibration of highest frequency which may be described as an oscillation of the two lattices of carbon atoms with respect to each other along one or another of the three cubic axes. The free vibrations of the structure in all these three modes have the same frequency, and this is known exactly from spectroscopic studies on the diffusion of monochromatic light in diamond. A sharply defined line with a frequency shift of 1332 cm^{-1} is recorded in the spectrum of the scattered light, and this frequency is associated with a vibration of the kind described above.

Whether the mode of vibration referred to above would be excited by the passage of X-rays through the crystal depends, as we have seen in part I, on whether this mode is or is not active in the absorption of infra-red radiation. The circumstances which determine whether a specified mode of vibration in a crystal is active or not in the absorption of infra-red radiation have been considered by various authors and will be found discussed in detail in several recent treatises. It is a well-established rule deduced from theory and confirmed experimentally that if a structure possesses centres of symmetry, any mode of vibration which manifests itself as a frequency shift in light scattering would be *inactive* in the absorption of infra-red radiation. In the first two sub-species of diamond referred to above, both sets of carbon atoms are dextro-carbon atoms or both laevo-carbon atoms respectively. It is clear that every point midway between a pair of atoms belonging respectively to the two lattices would in these cases be a centre of symmetry. Accordingly, in these two sub-species of diamond, since the mode of vibration with the frequency 1332 cm^{-1} manifests itself as a frequency in light-scattering, that mode would be *inactive* in infra-red absorption. *Per contra*, in the two other sub-species of diamond where the carbon atoms located at the points of the two lattices are of different species, the points midway between two carbon

atoms are *not* centres of symmetry. Hence the rule of mutual exclusion stated above is not applicable in their cases and hence the modes of vibration would be active *both* in the scattering of light and in the absorption of infra-red radiation. In what follows, we shall refer to the first two sub-species of diamond as the Oh I and Oh II types of diamond respectively, and the two other sub-species as Td I and Td II respectively. The use of these symbols has a special significance, viz., that the electronic structure of the first two species of diamond has the full or octahedral symmetry of the cubic system, whereas the electronic structure of the two other species has only the lower or tetrahedral symmetry.

We may conclude this section by a categorical statement of the results indicated by the theory. *In diamonds which belong to the two sub-species Oh I and Oh II, the fundamental vibration of the structure with frequency of 1332 cm^{-1} would not be active in infra-red absorption and hence the passage of X-rays through the crystal would not excite that vibration and hence would not result in a dynamic reflection. Per contra, in diamonds which belong to the two other sub-species Td I and Td II, the said vibration would be active in the absorption of infra-red radiation and hence the passage of X-rays through the crystal would excite those vibrations and give rise to dynamic reflections by the lattice planes in the crystal.*

4. The phase waves of dynamic reflection

We shall proceed to consider the nature of the dynamic reflections which may be expected to manifest themselves in the case of diamonds possessing only the lower or tetrahedral symmetry of electronic structure as the result of the excitation of the infra-red active vibration. As already stated, this vibration is an oscillation of the interpenetrating lattices of carbon atoms (in these cases dissimilar to each other) along one or another of the three cubic axes of the crystal. The atoms belonging to the two lattices appear in distinct but equidistant layers parallel to the cubic planes. The infra-red activity of the vibration arises from the fact that the electronic structure of the carbon atoms in the alternate layers is not completely identical. Hence, the oscillations of the two lattices with respect to each other results in periodic displacements of electric charge along the direction of vibration. We have three such movements to consider, which are respectively along one or another of the three cubic axes of the crystal. Hence, we have also three sets of phase-waves to consider whose normals are likewise the cubic axes.

The oscillatory movements of electric charge along the cubic axes of the crystal would necessarily also result in periodic movements of the stratifications of electric charge which appear in the crystal in other directions. In considering the question whether these movements would give rise to dynamic reflections by those stratifications, we have to remark that movements *parallel* to any set of stratifications cannot give rise to any dynamic reflections by them; only movements *normal* to the stratifications can give rise to such reflections, and

hence if the actual movements are *inclined* to the stratifications, we need consider only the components of the movement along their normals.

Considering for example the (111) planes in a crystal, the three movements respectively along the three cubic axes are equally inclined to those planes, and hence the magnitude of all the three components resolved along the normal to the (111) planes would be diminished to the same extent. Hence, in general, *the (111) planes would give three dynamic reflections* which in appropriate circumstances may be expected to be of comparable intensities. On the other hand, the (220) planes of the crystal contain one cubic axis and are equally inclined to the other two at angles of 45° . The displacements of electric charge parallel to the first axis and hence also parallel to the plane of the stratifications would not give rise to any dynamic reflection. However, movements along the two other cubic axes would result in a displacement of the stratifications in the (220) planes diminished to equal extents by reason of their inclination to those planes. We conclude that *the (220) planes would give only two dynamic reflections* which in appropriate circumstances would be of equal intensity. Considering again the (400) planes, these contain two of the cubic axes and are normal to the third, and it follows for similar reasons that *the (400) planes give only one dynamic reflection*. The fact that the phase-waves are parallel to those planes has a further interesting consequence to which we shall revert later. Finally, we may briefly consider the (311) planes. These planes are equally inclined to two of the cubic axes at small angles and are nearly perpendicular to the third. The dynamic reflections due to the first two movements may therefore be expected to behave very differently from the third.

5. The geometry of the dynamic reflections

The general method already indicated in part I enables us to picture the configuration of the dynamic reflections given by the various lattice planes in the crystal. We shall here content ourselves with the consideration of the dynamic reflections associated with the (111), (220), (311) and (400) planes, since these are the four largest spacings in the crystal which also reflect X-rays with notable intensity. The first three cases are represented in figures 1, 2 and 3 respectively for settings of the crystal so chosen that the characteristic features of each case are brought out clearly. The primary X-ray beam is assumed to traverse the crystal horizontally and its direction is indicated by arrows at the points of entry and exit on a sphere. The plane of incidence on the lattice-spacings is also assumed to be horizontal and is indicated by a great circle drawn on the surface of the sphere. The normal to the lattice spacings accordingly appears as a point on the same great circle with an arrow attached to it and directed radially outwards. The three cubic axes of the crystal which are the normals to the phase-waves of dynamic reflection are represented on the sphere in a similar fashion, the points where they appear being determined by the chosen setting of the crystal. Three great circles

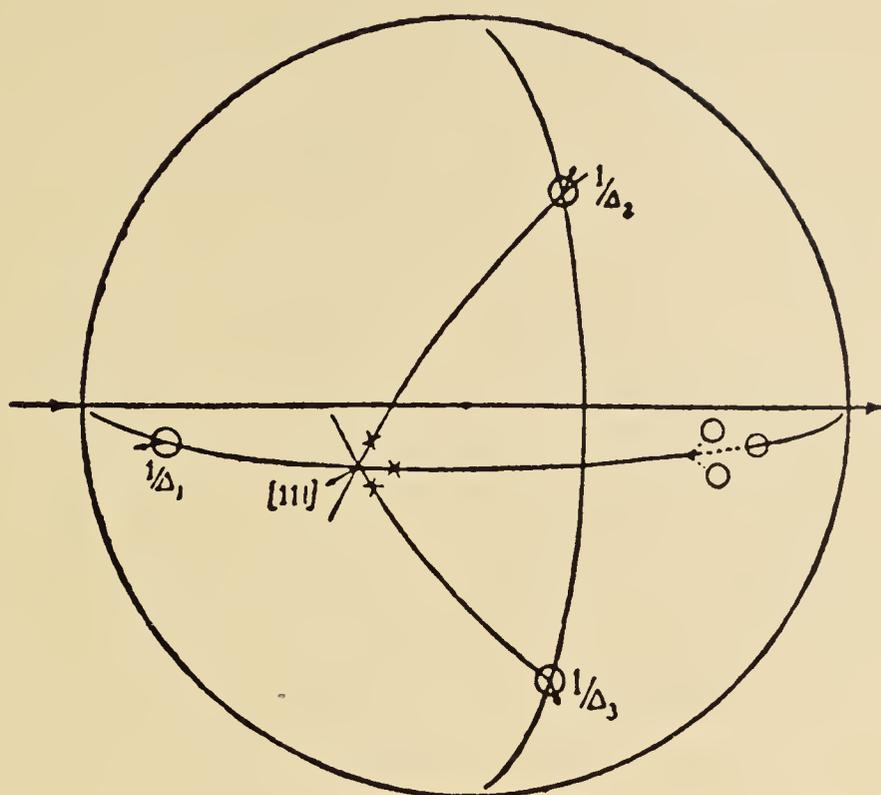


Figure 1. Dynamic reflections by the (111) planes.

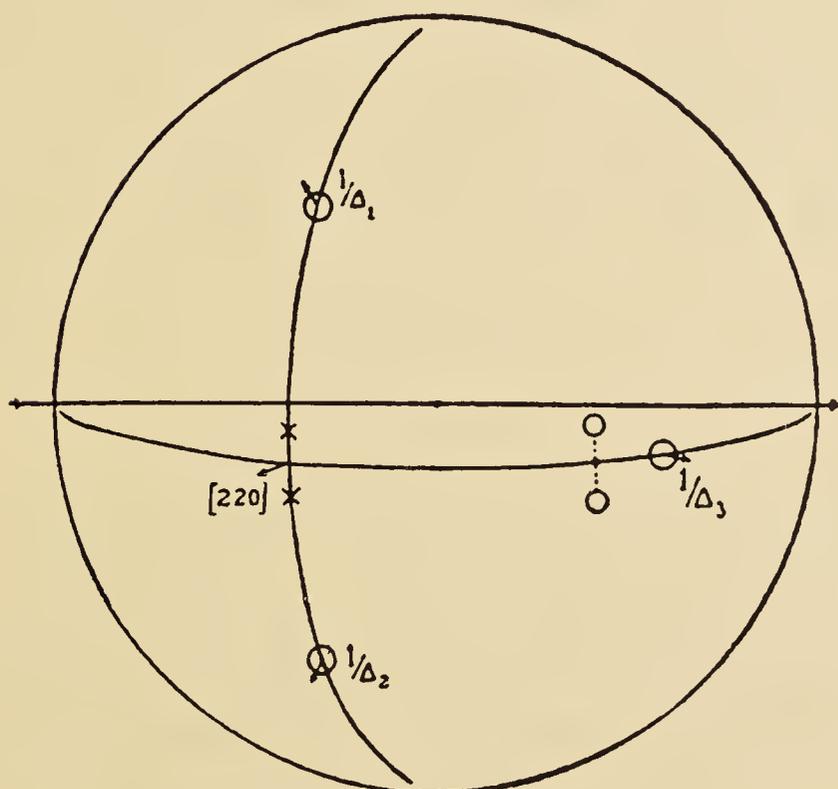


Figure 2. Dynamic reflections by the (220) planes.

are also drawn each of which contains one of the phase-wave normals and the normal to the lattice spacings. In each case the setting of the crystal chosen is such that one of the great circles coincides with the plane of incidence. The normals to the three sets of dynamic stratifications would necessarily lie on these three great

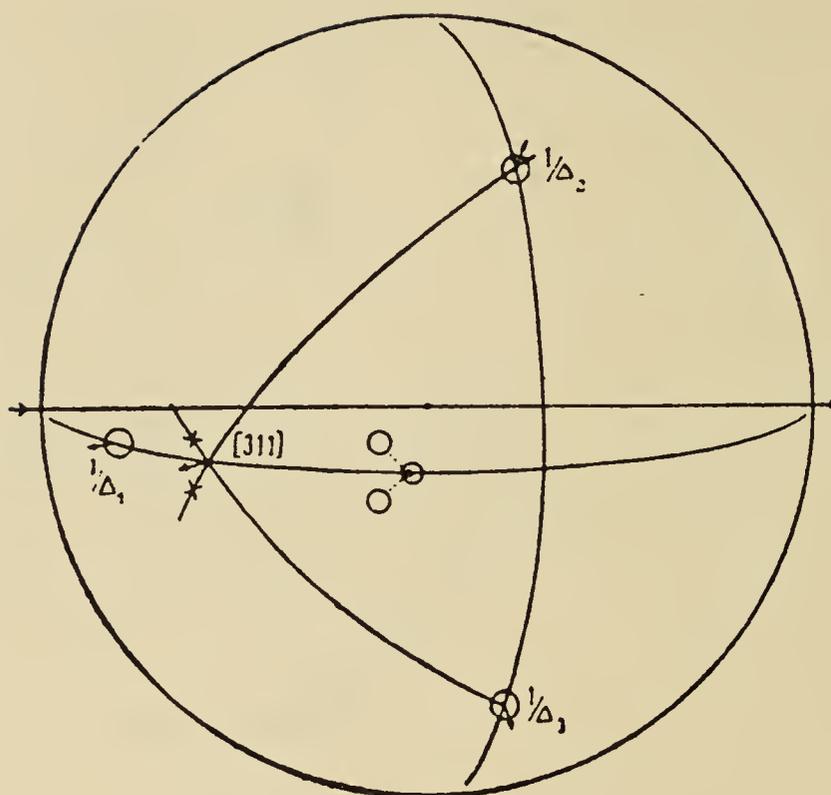


Figure 3. Dynamic reflections by the (311) planes.

circles. The positions of the dynamic reflections would be determined by drawing three other great circles, each containing the direction of the incident beam and the normal to the particular dynamic stratification, and marking off on these circles, points such that the angle of reflection is equal to the angle of incidence in the respective planes. The entire procedure is that indicated by the theory of dynamic reflection developed in part I and contained in the two equations

$$\frac{\vec{1}}{D} = \frac{\vec{1}}{d} + \frac{\vec{1}}{\Delta} \quad (1)$$

$$2D \sin \psi = \lambda. \quad (2)$$

For a particular X-ray wavelength determined by the lattice spacings and the angle of incidence of the X-rays on them, we would observe the ordinary or unmodified reflection in the plane of incidence. The direction in which this appears is represented in each of the figures as another point on the equatorial circle. For the same X-ray wavelength, the dynamic reflection or reflections permitted would also appear in the same direction superposed on the ordinary or static reflection. For other X-ray wavelengths, the static reflection ceases to appear but the dynamic reflections would persist, their directions being determinable in the manner already explained. The phase wavelength is infinite for the particular case in which the static and dynamic reflections are superposed. With progressively changing X-ray wavelength, $1/\Delta$ would increase in numerical magnitude and the point on the sphere representing the dynamic stratification would move out in one direction or another along the great circle which defines its path. The construction already indicated would then result in giving positions

to the dynamic reflections differing from that in which they were originally coincident. In the particular settings of the crystal which have been chosen for drawing the figures, the dynamic reflection which corresponds to the cubic axis in the plane of incidence would—if it exists at all—appear in the plane of incidence, while the other two would swing out of that plane symmetrically on either side.

For reasons already explained, whereas the (111) planes show *three* dynamic reflections in the setting indicated, the (220) planes show only two reflections: these are displaced laterally, one on either side. The third reflection lying in the plane of incidence though *geometrically* permitted is *physically* excluded by reason of the movement of the stratifications being in their own plane. The case of (400) reflection is of special interest. As explained earlier, only one dynamic reflection is possible in this case and since the phase-waves which give that reflection are parallel to the stratifications themselves, the dynamic reflection for all X-ray wavelengths would appear in the same direction, viz., that indicated by the ordinary law of geometric reflection.

6. Summary

Considerations of the physical nature of the directed valences of the tetrahedral carbon atom lead to the conclusion that there are two possible states of the carbon atom, viz., a dextro-state and a laevo-state corresponding respectively to the two possible senses of the orbital angular momentum of the electrons about their tetrahedral valence directions. From this again it follows that a homogeneous diamond crystal may have an electronic structure which has either the highest or octahedral symmetry or else only the lower or tetrahedral symmetry of the cubic system. In diamonds having octahedral symmetry, the oscillations of the two carbon atoms with respect to each other would be inactive in the absorption of infra-red radiation, whereas in diamonds of which the electronic configuration has tetrahedral symmetry that vibration would be active in such absorption. From this it follows that only with diamonds of the latter type would the X-rays excite the lattice vibrations and exhibit the dynamic reflections consequent thereon. The vibrations excited and their phase-wave-normals are parallel to the three cubic axes of the crystal. It follows that whereas the (111) planes would exhibit *three* dynamic reflections at any one setting of the crystal, the (220) would exhibit only *two* and the (400) planes only *one*.

The diffraction of X-rays by diamond—Part III

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1. Introduction

In the first part of the present memoir, it was shown from theoretical considerations of a very general nature that when X-radiations traverse a crystal, their passage could result in exciting vibrational transitions in the energy levels of the crystal and as a consequence of such excitation lead to a reflection of the incident X-rays by the lattice planes of the crystal with a change of frequency. The theory indicated it as an essential condition for such a process to occur that the vibrational transitions in question are effective as absorbers of infra-red radiation of the appropriate frequency. The phenomenon here envisaged is quantum-mechanical in its nature; in other words, vibrational transitions would be excited and would be accompanied by X-ray reflections of altered frequency even when the frequency of the vibrations is so high that they would not be thermally excited to any appreciable extent. However, considerations of a purely classical nature assist in elucidating the nature of the phenomenon and in deducing its observable features. The infra-red activity of a vibrational mode in a crystal arises because it involves a periodic displacement of the electronic clouds in the crystal with the same frequency; such a displacement would result in an oscillation of the stratifications of electron density which reflect the X-rays traversing the crystal and hence also lead to dynamic reflections of altered frequency.

Perhaps the most striking feature of the theory expounded in part I is the connection which it indicates between the behaviour of a crystal in X-ray diffraction and the activity of the modes of its internal vibration in the absorption of infra-red radiation. The particular case of diamond is of special interest in this connection. For, as was shown in part II of the memoir, theoretical considerations indicate that diamonds should be forthcoming in forms which differ in the inner symmetry of their electronic configuration and hence also in their infra-red behaviour. The detailed discussion showed that the diamonds of which the inner symmetry is octahedral would *not* exhibit dynamic X-ray reflections, whereas those diamonds of which the symmetry is tetrahedral would exhibit such reflections. In other words, the case of diamond enables us to put the relation

between X-ray diffraction and infra-red activity to a direct experimental test. Further, it was also shown in part II of the memoir that in the case of diamond, we are concerned with three modes of vibration which are respectively parallel to the three cubic axes of the crystal and hence variously inclined to the lattice-spacings in it. As a result, the dynamic reflections by these spacings differ both in their number and in their geometric configuration in a highly characteristic fashion. Thus, the application of the general theory to the particular case of diamond furnishes us with abundant material for comparison with the facts of experiment.

2. The tetrahedral and octahedral forms of diamond

Three diamonds employed in the present investigation are represented in plate I. The first is a cleavage plate parallel to the (111) spacings of the crystal. The second is a flat tabular crystal in its natural form as a hexagonal plate with faces parallel to the (111) planes. The third is a thin faceted plate of diamond with its faces nearly parallel to the (111) planes. All three diamonds are perfectly colourless, without any visible cracks or inclusions in their interior and obviously of the highest quality. Nevertheless, the first two diamonds differ enormously in their physical behaviour from the third, as is apparent from a comparison of the photographs reproduced in the plate. We proceed to explain how these photographs were obtained.

The photographs on the left-hand side were recorded by placing the diamond against a fluorescent screen. (This was a slab of lithium fluoride crystal impregnated with a little uranium oxide.) The λ 2537 radiation from a water-cooled magnet-controlled mercury arc in quartz was isolated by a monochromator and allowed to fall on the diamond and then on the LiF-UO₂ screen placed behind it, and the fluorescence excited in the latter was photographed from the rear. The photographs on the right-hand side of the plate were obtained in a very simple manner. The diamond was placed between two crossed polaroids and photographed as seen through them against a bright source of light. It is seen from the photographs reproduced in plate I that *the cleavage plate and the tabular crystal are both perfectly opaque to the λ 2537 radiations of the mercury arc and that they exhibit not a trace of birefringence, in other words that they are truly and perfectly isotropic crystals. On the other hand, the thin faceted plate is completely transparent to the λ 2537 radiations of the mercury arc, but it exhibits a feeble but nevertheless readily observable birefringence pattern with definite geometric features related in their orientation to the structure of the crystal.*

Diamond is, in effect, a giant macromolecule of carbon. Hence a specimen of it which exhibits no detectable birefringence, or, in other words, is optically homogeneous, may, *prima facie*, be expected to make a close approach to the ideal state of crystal perfection. *Per contra*, a specimen of diamond—which

exhibits over its entire area, a geometric pattern of birefringence however feeble it may be in intensity—must necessarily be regarded as very remote from such ideality. A striking confirmation of the correctness of these remarks is furnished by the results of a simple experimental test in which the diamonds figured in plate I were used as X-ray spectrometers to resolve the $K\alpha_1$ and $K\alpha_2$ radiations from a copper target. The X-ray beam from the target diverged through a fine slit and fell on the diamond in an appropriate setting placed at a distance of 5 cm from the slit. The surface reflection of the X-rays by the (111) planes of the crystal was recorded on a photographic film held at a distance of about 100 cm. The spectrograms recorded with the flat tabular diamond and by the faceted plate are reproduced as figures 1(a) and 1(b) respectively in plate II. A very great difference between the two diamonds in regard to the degree of their crystal perfection is indicated by the difference in the two spectrograms. But the actual difference is even greater. For, the width of the $K\alpha_1$ and $K\alpha_2$ lines as recorded in figure 1(a) in plate II represents the natural spectral widths of these radiations and is therefore not a true measure of the crystal perfection of the tabular diamond. To obtain a true measure of that perfection, it is necessary to adopt a spectrographic technique in which two crystals of diamond are employed. The results of that technique are depicted in the series of spectrograms reproduced as figures 2(a), (b), (c) and (d) of plate II and figures 1(a), (b) and (c) of plate X. We shall revert to the details of the technique and the significance of the results obtained with it in a subsequent section of the present paper.

Studies on the infra-red absorption spectra of diamond have established the fact that diamonds which are completely transparent to the $\lambda 2537$ radiations of the mercury arc in the ultra-violet are also completely transparent to infra-red radiations over the entire range of the characteristic frequencies of vibration of the structure of diamond ranging from 1332 cm^{-1} downwards to longer wavelengths. *Per contra*, the diamonds which are opaque to the $\lambda 2537$ radiations also exhibit a marked absorption over that entire range of infra-red wavelengths. It is thereby established that diamonds of the former kind possess an inner electronic configuration which has the full or octahedral symmetry of the cubic system, whereas the diamonds of the latter kind possess an electronic configuration which possesses the lower or tetrahedral symmetry of that system. The remarkable fact that diamonds with a lower degree of symmetry are highly perfect crystals while those with a higher degree of symmetry are highly imperfect receives a natural explanation on the basis of the theory of the structure of diamond expounded in part II of the memoir. As there explained, the tetrahedral diamonds are those in which each dextro-carbon atom is linked to four laevo-carbon atoms and likewise each laevo-carbon atom is linked to four dextro-carbon atoms. *There is thus no physical difference between the two sub-species Td I and Td II* of the tetrahedral class of diamonds but only an interchange in the description of the two lattices which constitute the structure. On the other hand, the octahedral type of diamonds consists entirely of dextro-carbon atoms or

entirely of laevo-carbon atoms; *the two sub-species Oh I and Oh II are therefore physically different*. These circumstances are clearly favourable for the Td diamonds exhibiting a high degree of homogeneity and for the Oh diamonds to be markedly heterogeneous in their texture. But there is another and a deeper consideration which has also to be borne in mind. When a dextro-carbon atom is linked to a laevo-carbon or vice versa, the two electrons shared between them describe their orbits about the valence direction in the same sense. On the other hand, when a dextro-carbon atom combines with a dextro-carbon atom, or a laevo-carbon atom with a laevo-carbon atom, the shared electrons describe their orbits about the common valence direction in opposite senses. It would seem that a homogeneous structure extending through large volumes would be more likely to appear in the former case than in the latter.

It is appropriate at this stage to remark that it is the perfect diamonds belonging to the tetrahedral class that exhibit the phenomena of dynamic reflection of X-rays, while it is the imperfect diamonds of the octahedral type that do not show those phenomena. This is in agreement with the indications of the theory developed in part II of the memoir. But it is necessary to demonstrate that the failure of the octahedral diamonds to exhibit dynamic reflections is not ascribable to their imperfection of structure, but is a consequence of their inactivity in infra-red absorption. We shall revert to this presently.

3. Dynamic X-ray reflections and crystal symmetry

Figure 1 in plate III is a Laue photograph of a cleavage plate of diamond whose faces are parallel to the (111) planes of the crystal. The crystal was set exactly normal to a fine pencil of X-rays from a copper target. The picture shows perfect trigonal symmetry not only with regard to the ordinary or Laue reflections but equally also with regard to the dynamic reflections appearing in the vicinity of the hexagonal corners of the print adjacent to the intense (111) Laue spots. Figure 2 in plate III is a similar photograph taken in similar circumstances with a crystal of diamond which exhibits twinning of the spinel type. It will be seen that this pattern exhibits hexagonal symmetry in all its features, including especially the dynamic reflections which are seen at all the six corners of the hexagonal print. The fact clearly evident from figures 1 and 2 in plate III that the dynamic X-ray reflections of diamond exhibit the symmetry of the crystal in the same manner and to the same extent as the static reflections is obviously of the highest significance. Taken in conjunction with the circumstance that the diamonds which exhibit the dynamic reflections are perfect and indeed—as will appear presently—are ideal crystals, it demonstrates the correctness of the view expressed by the author in the original publication of the year 1940 that these phenomena exhibited by diamond are fundamental in their nature and of the highest importance in relation to the theory of X-ray diffraction in crystals.

As already remarked earlier, the fact that the dynamic reflections are not manifested by the diamonds of octahedral symmetry is a confirmation of the theoretical ideas set out in part I of the memoir. But the circumstance that these diamonds are imperfect tends to create some doubt in the matter. Very frequently, indeed, diamonds of this class give distorted Laue patterns. Hence a critical observer might be disposed to infer that it is this imperfection rather than the inactivity in infra-red absorption which is responsible for the non-appearance of the dynamic reflections. To dispel such an impression, it is necessary to investigate the matter with carefully selected material. The intensity of the birefringence exhibited by these diamonds is a measure of the imperfections in their structure. It is therefore desirable to select a specimen in which such birefringence is of extremely low intensity. The specimen illustrated in figures 3(*a*) and 3(*b*) in plate I was found to be the best available in this respect. Even so, the mosaicity of its structure exhibits itself in a notable enhancement of the intensity of the Laue spots in its diffraction patterns. Such enhancement is particularly striking in the case of spots that are only feebly recorded with diamonds of the tetrahedral class. Even such a weak effect as the diffuse X-ray scattering due to thermal agitation is recorded with greatly enhanced intensity by this specimen. But there is no observable distortion of the Laue spots, and had the dynamic reflections been present, they would have been very striking features in the recorded patterns. Actually, not a trace of them is observable in figures 1(*b*) and 1(*d*) in plate VIII which were recorded with this diamond in appropriate settings. For the sake of comparison, the patterns recorded with the tetrahedral diamond in identical settings are reproduced as figures 1(*a*) and 1(*c*) side by side with them in the same plate VIII.

4. Observable features of the dynamic reflections

The following special points are worthy of mention:

- I. As the dynamic reflections by diamond are a consequence of the excitation by the incident X-rays of an infra-red vibration of high frequency, variations of temperature within wide limits should be entirely without effect either on the intensity or the sharpness of these reflections.
- II. As a result of the crystal perfection of diamond, the ordinary reflections of monochromatic X-rays would demand a very precise setting of the crystal for their observation, on either side of which they would disappear completely. The dynamic reflections would coincide with the static reflections at the correct setting, but would not disappear when the setting is altered. Their intensity would however fall off rapidly as the crystal is moved away from the correct setting in their direction.
- III. The dynamics of the excited vibration in diamond demands that the phase-waves which determine the direction in which the dynamic reflections appear

are precisely normal to one or another of the cubic axes of the crystal. As a consequence, the reflections would be very sharply defined, being indeed in this respect almost comparable with the static reflections.

IV. By making observations of the directions in which the dynamic reflections appear, it is possible to determine the orientation of the phase-waves. The most suitable arrangement for such determination is to place the crystal so that one of the cubic axes lies in the plane of incidence of the X-rays on the (111) planes, and then to alter the setting in such manner that the plane of incidence does not change. The geometric law of dynamic reflection takes a very simple form in this case and a precise measurement of the orientation of the phase-waves becomes possible.

The various special features referred to above were all fully established by the observations made by the author and his collaborators in the months following the original publication of April 1940. Detailed reports of those studies appeared in the *Proceedings of the Indian Academy of Sciences* in the years 1940 and 1941. It would be superfluous here to traverse the same ground or to comment on the literature of a controversial nature published from other laboratories on the subject then and subsequently. To make the present memoir complete, however, a series of photographs showing the dynamic reflections by the (111) planes, (220) planes, (311) planes and (400) planes of diamond in various settings are reproduced as plates IV, V, VI, VII, VIII and IX accompanying the present paper. A comparison of the features noticed in this series of photographs with the theoretical diagrams given in part II of the memoir will show how complete the agreement is between fact and theory.

5. Spectral analysis of X-ray diffraction

We now return to a detailed description of the technique which enables a spectroscopic analysis to be made of the X-ray diffraction phenomena exhibited by diamond. The general nature of this technique to which a brief reference was made earlier will be evident from figure 1 (text). A powerful source of X-rays from a copper target passes first through a wide slit and then through the diamond under study. The rays *internally* diffracted by the (111) planes of this diamond are restricted by a fine slit through which they pass before they are incident on the surface of a second perfect diamond which functions as a spectrometer. The rays reflected *externally* by the second diamond are received and recorded on a photographic film placed at a distance of 100 cm. The actual technique consists in rotating the first diamond in steps through very small angles over a total range of a few minutes of arc. What is actually recorded on the photographic film is the spectrum of X-radiation in the narrow range between the $K\alpha_1$ and $K\alpha_2$ lines and perhaps a little more on either side of them.

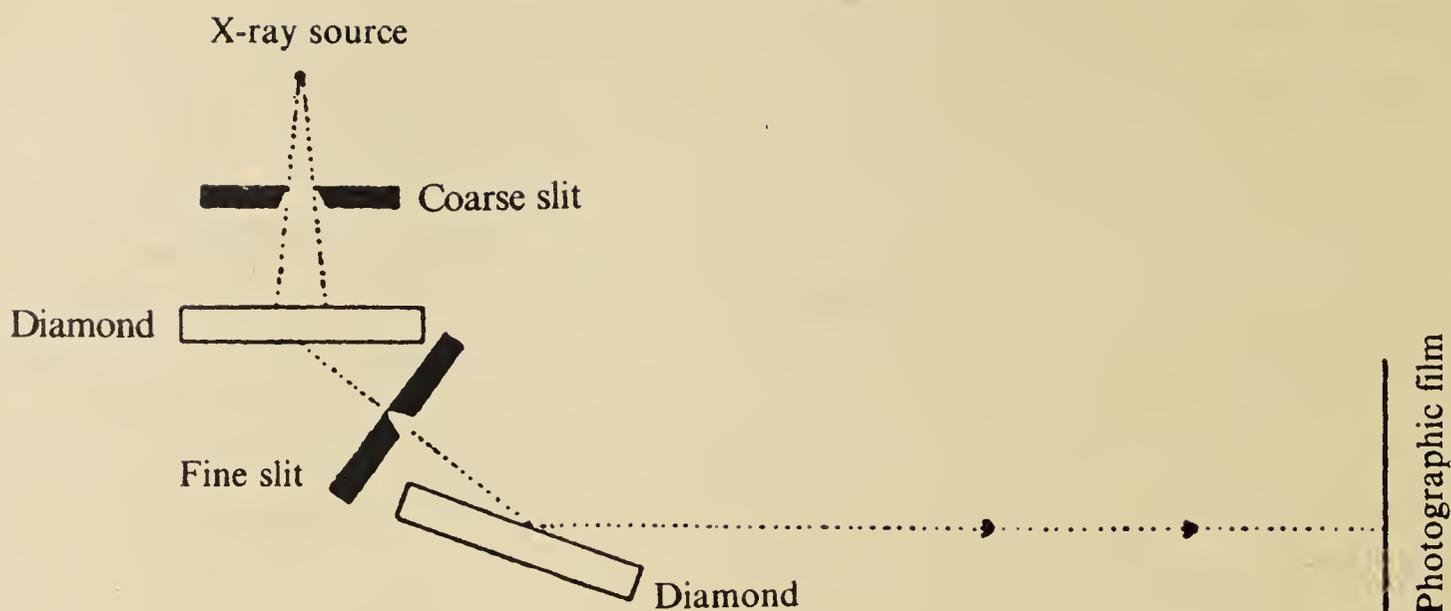


Figure 1

The nature of the results obtained will be evident from a scrutiny of the series of spectrograms reproduced as figures 2(a), (b), (c) and (d) in plate II and the three others which appear as figures 1(a), (b) and (c) in plate X. The latter three have been enlarged so as to be readily comparable with the single crystal spectrogram appearing as figure 1(a) in plate II. The most significant feature of the series of spectrograms is the appearance of an extremely sharp line which drifts in its position as the diamond is rotated. The spectral width of this sharp line is not more than about a tenth of the natural width of the $K\alpha_1$ or the $K\alpha_2$ radiations. It represents the super-monochromatic radiation manufactured by the first diamond from the incident white radiation by Laue reflections at the (111) stratifications. Its extreme sharpness reflects the extraordinary perfection of the diamond.

It will be seen that the relative intensities of the $K\alpha_1$ and $K\alpha_2$ lines differ enormously in the different spectrograms. That they persist over the whole range of settings of the diamond clearly shows that they represent the dynamic reflections of the $K\alpha_1$ and the $K\alpha_2$ radiations by the (111) planes of the first diamond. The static reflections of those radiations are recorded only at the precise settings at which those reflections are possible.

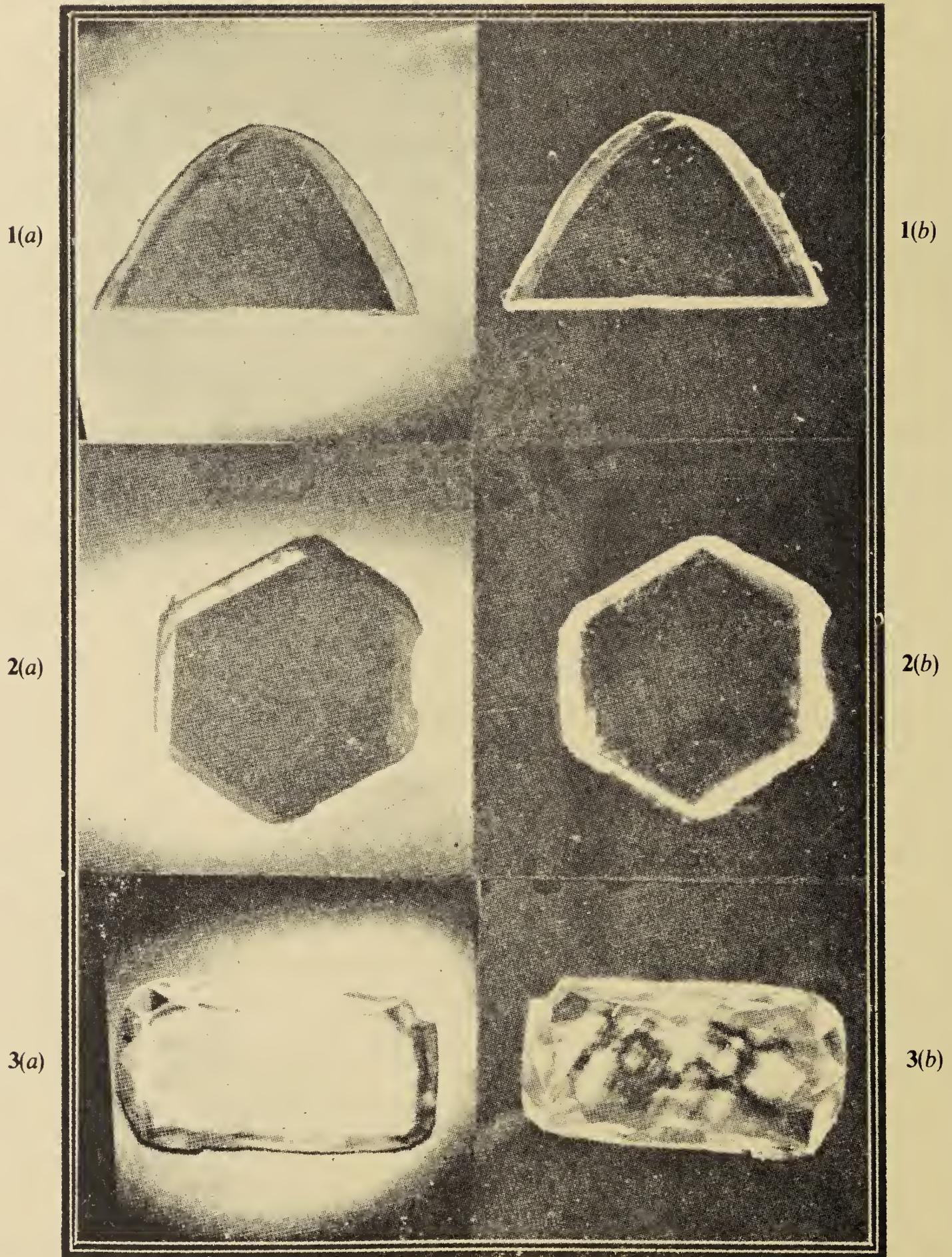
6. Acknowledgements

The Laue patterns reproduced in plates III, IV, V, VI, VII, VIII and IX, as well as the single-crystal and double-crystal X-ray spectra reproduced in plates II and X accompanying this memoir were recorded in the X-ray Laboratory of the Raman Research Institute by the Assistant Director of the Institute, Professor A Jayaraman, for whose valuable co-operation in the research the

author of this memoir is greatly indebted. The gift to the Institute of a rotating target X-ray set by Sri Purushottamdas Thakurdas made the work possible.

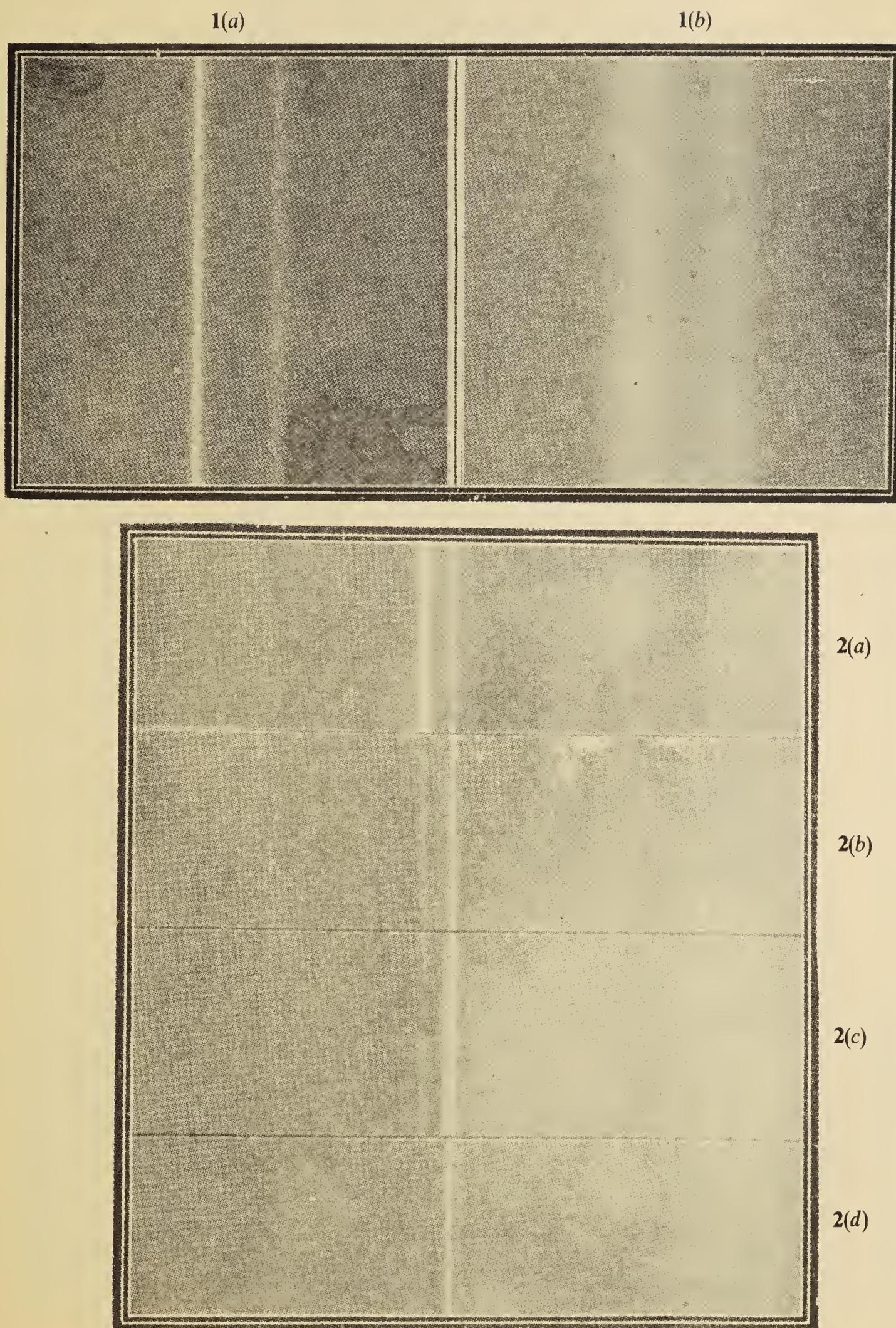
7. Summary

Studies on the crystal perfection of diamond by single-crystal and double-crystal X-ray spectroscopic methods demonstrate that the non-birefringent diamonds which are infra-red active and possess only tetrahedral symmetry in their electronic configuration are extraordinarily perfect and are indeed ideal diamonds. It is these diamonds that exhibit the phenomena of dynamic reflection of X-rays. The detailed studies of the phenomena show that the experimental facts of the subject are completely in agreement with the results of the theory expounded in the first two parts of the memoir. The non-appearance of the dynamic X-ray reflections with the diamonds which have an octahedral symmetry of electronic configuration is shown to be consequential on these diamonds being inactive in the absorption of infra-red radiation.

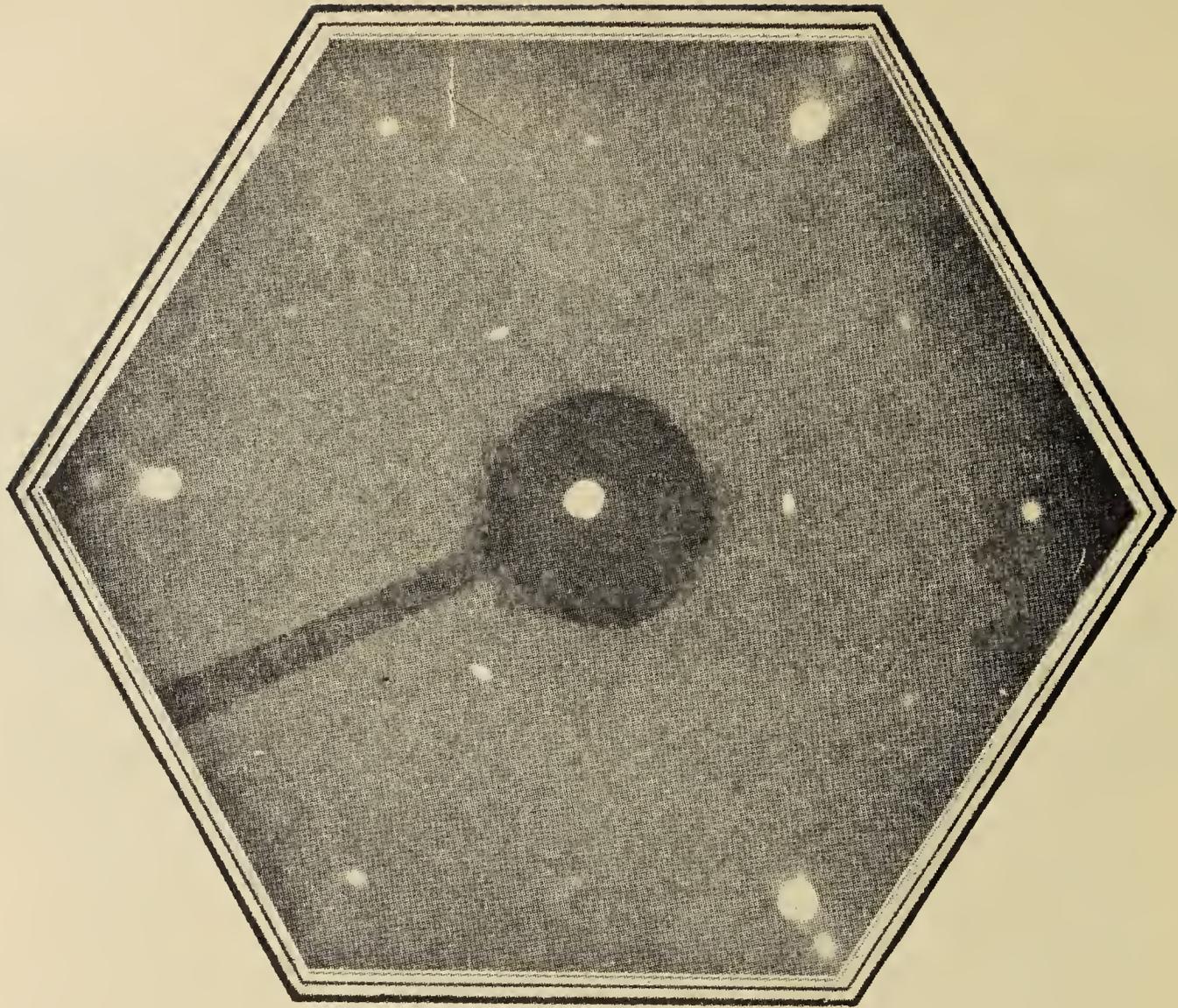


Figures 1(a), (b) 3(a), (b)

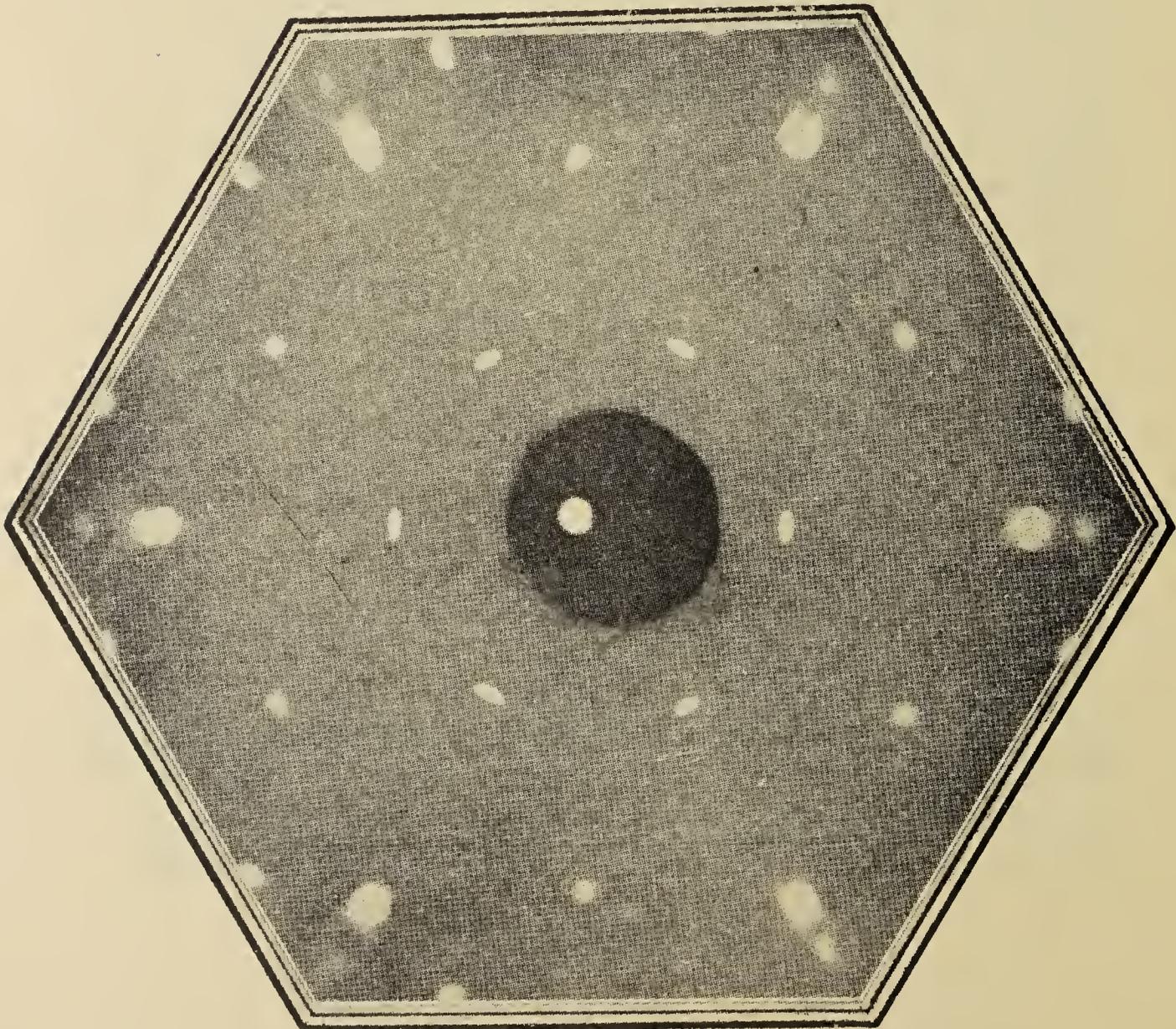
Plate I



Figures 1(a), (b) and 2



(1)



(2)

Figures 1 and 2

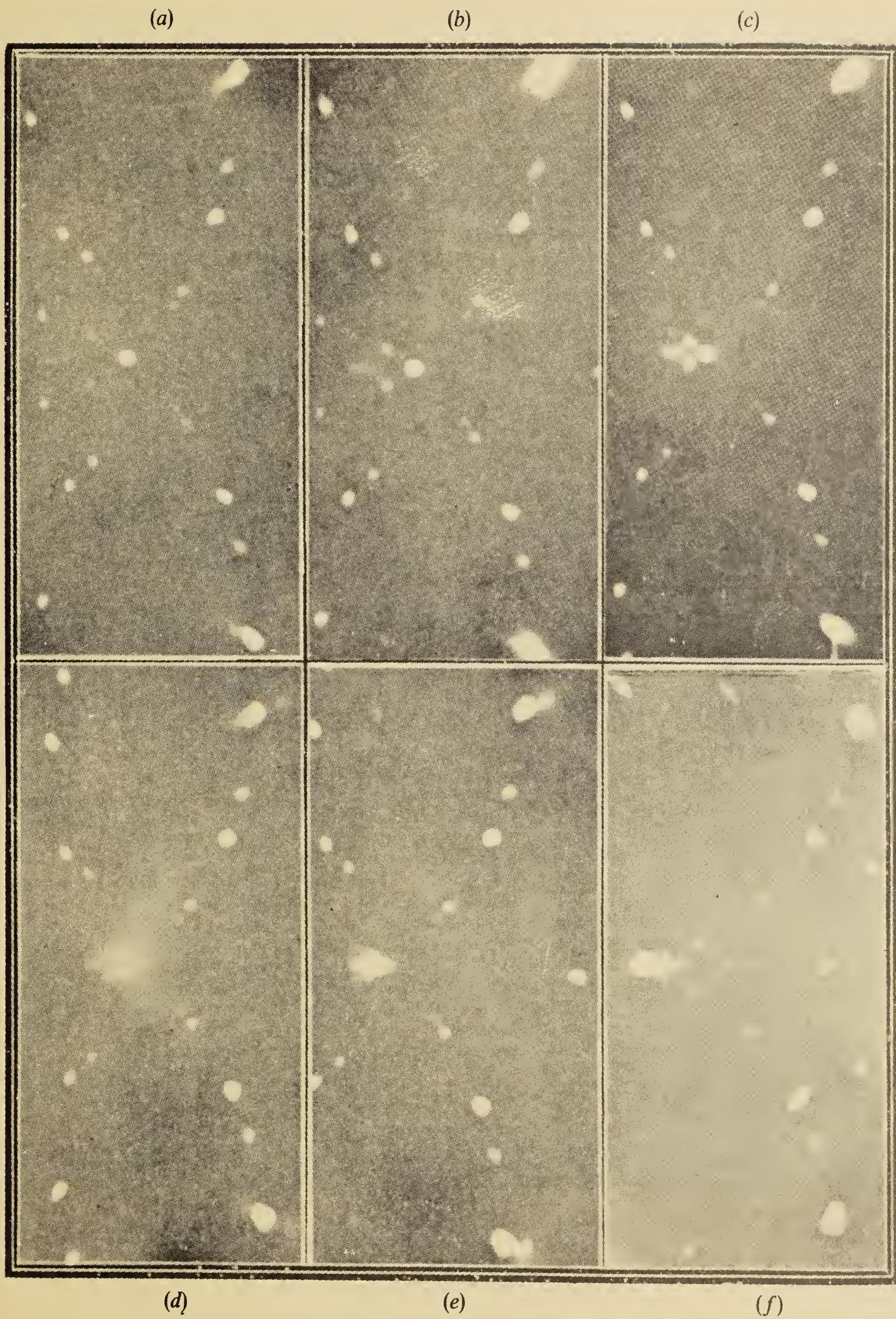


Figure 1. Exhibiting the dynamic reflections by the (111) planes of various settings.

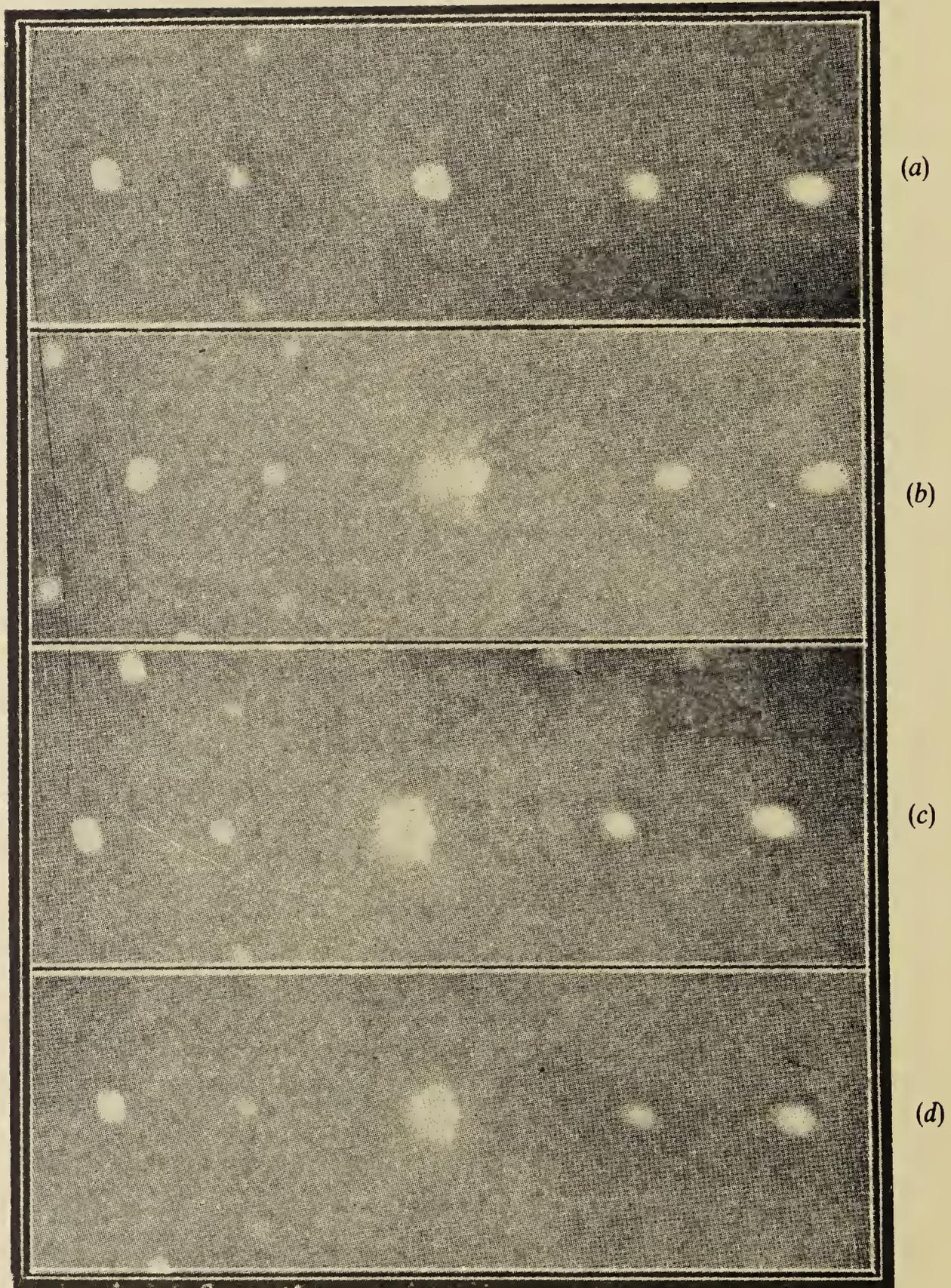


Figure 1. Exhibiting the dynamic reflections by the (220) planes at various settings.

Plate V

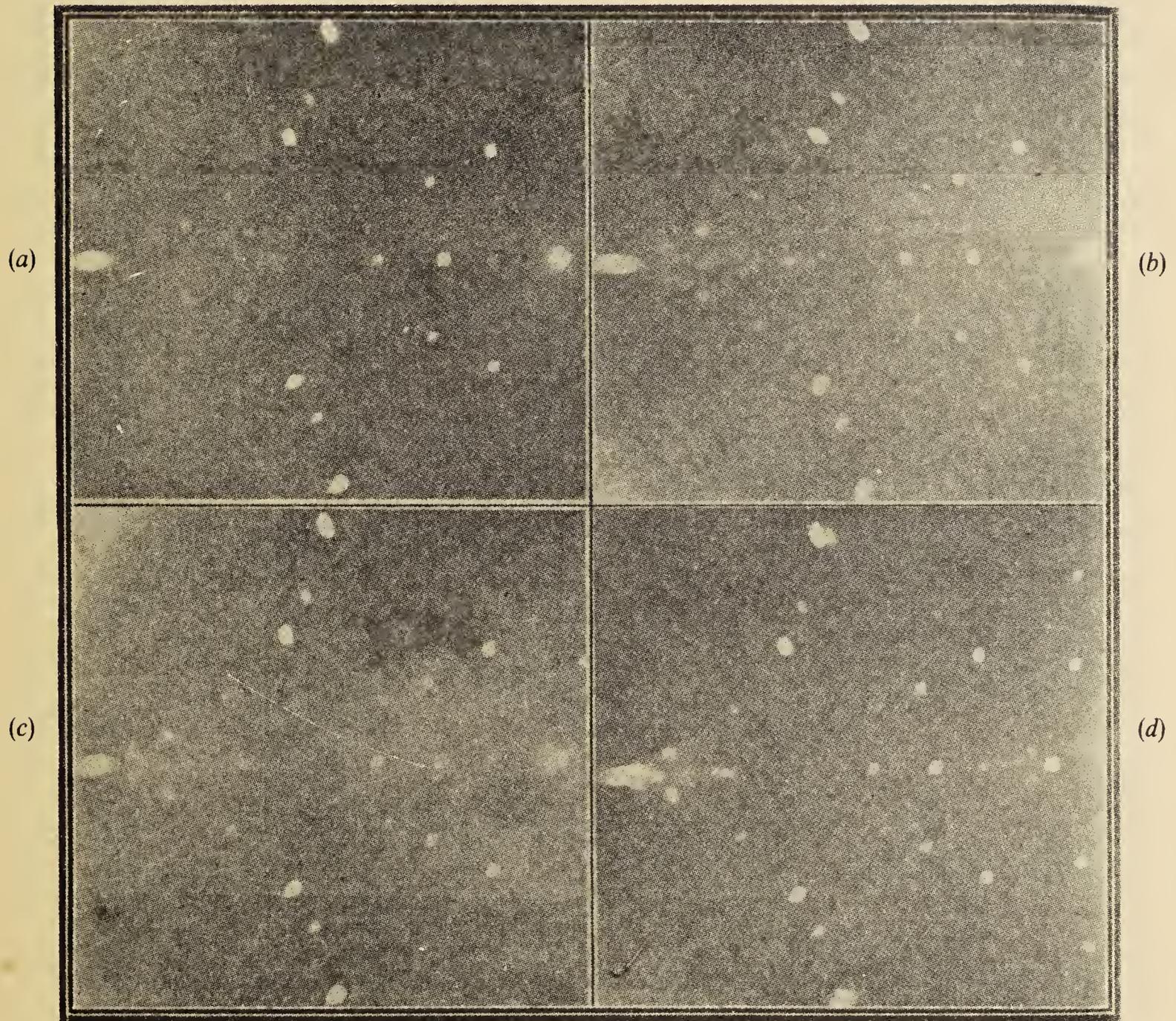


Figure 1. Exhibiting the dynamic reflections by the (111) planes at the left and by the (113) planes at the right.

Plate VI

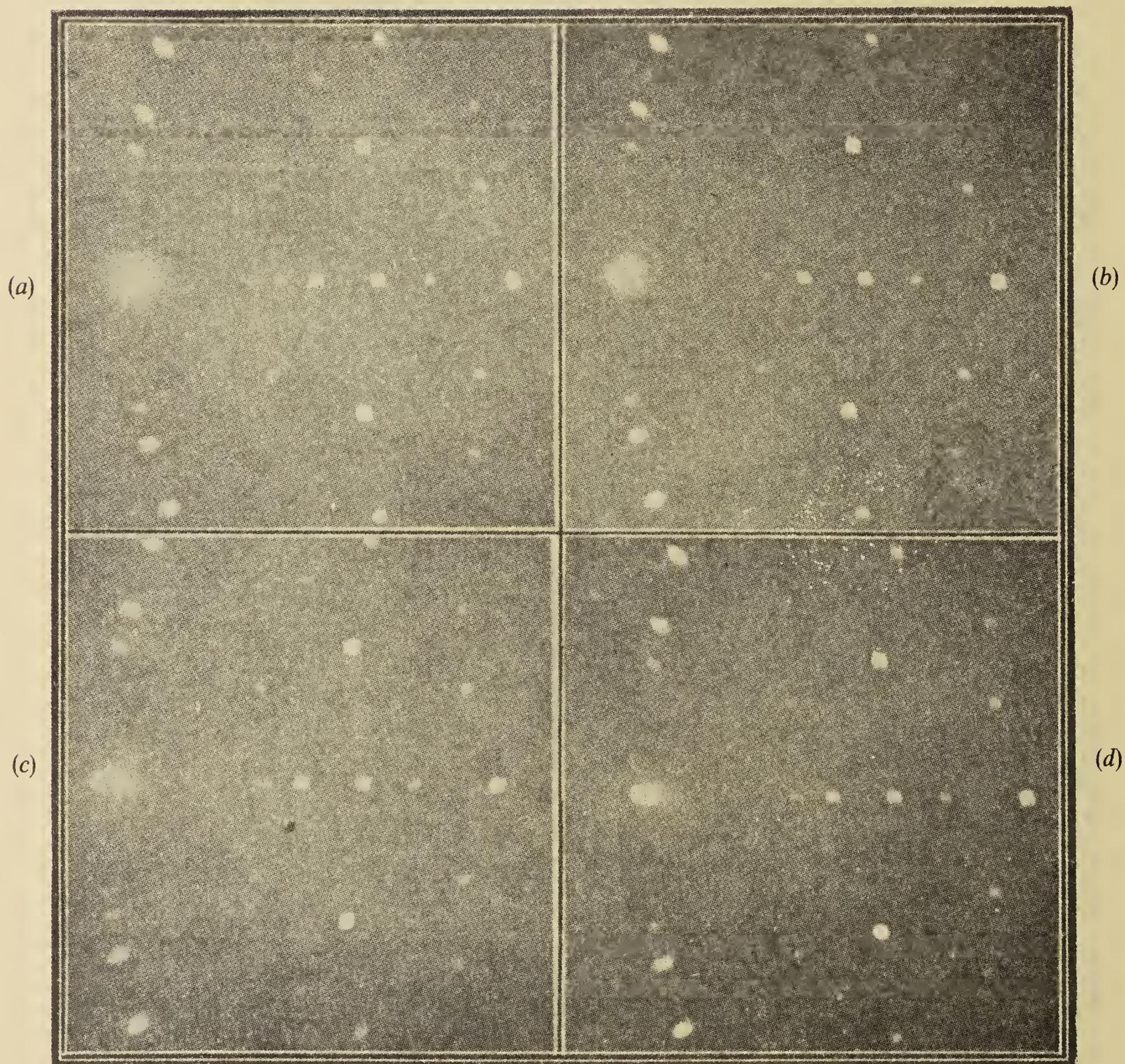


Figure 1. Exhibiting the dynamic reflections by the (400) planes at the left.

Plate VII

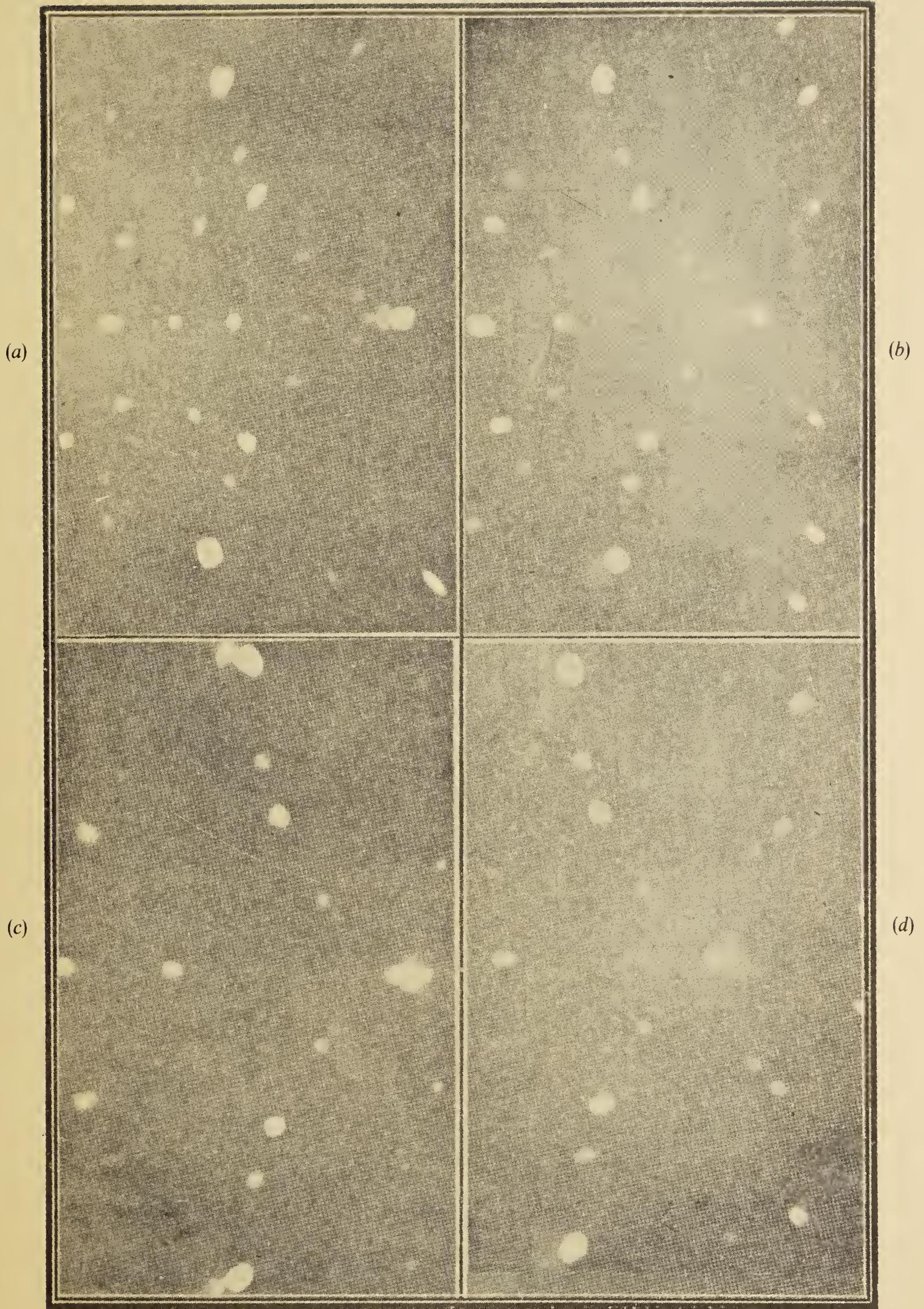


Figure 1. Exhibiting the dynamic reflections by the (111) planes of tetrahedral diamond on the left and their absence with octahedral diamond on the right.

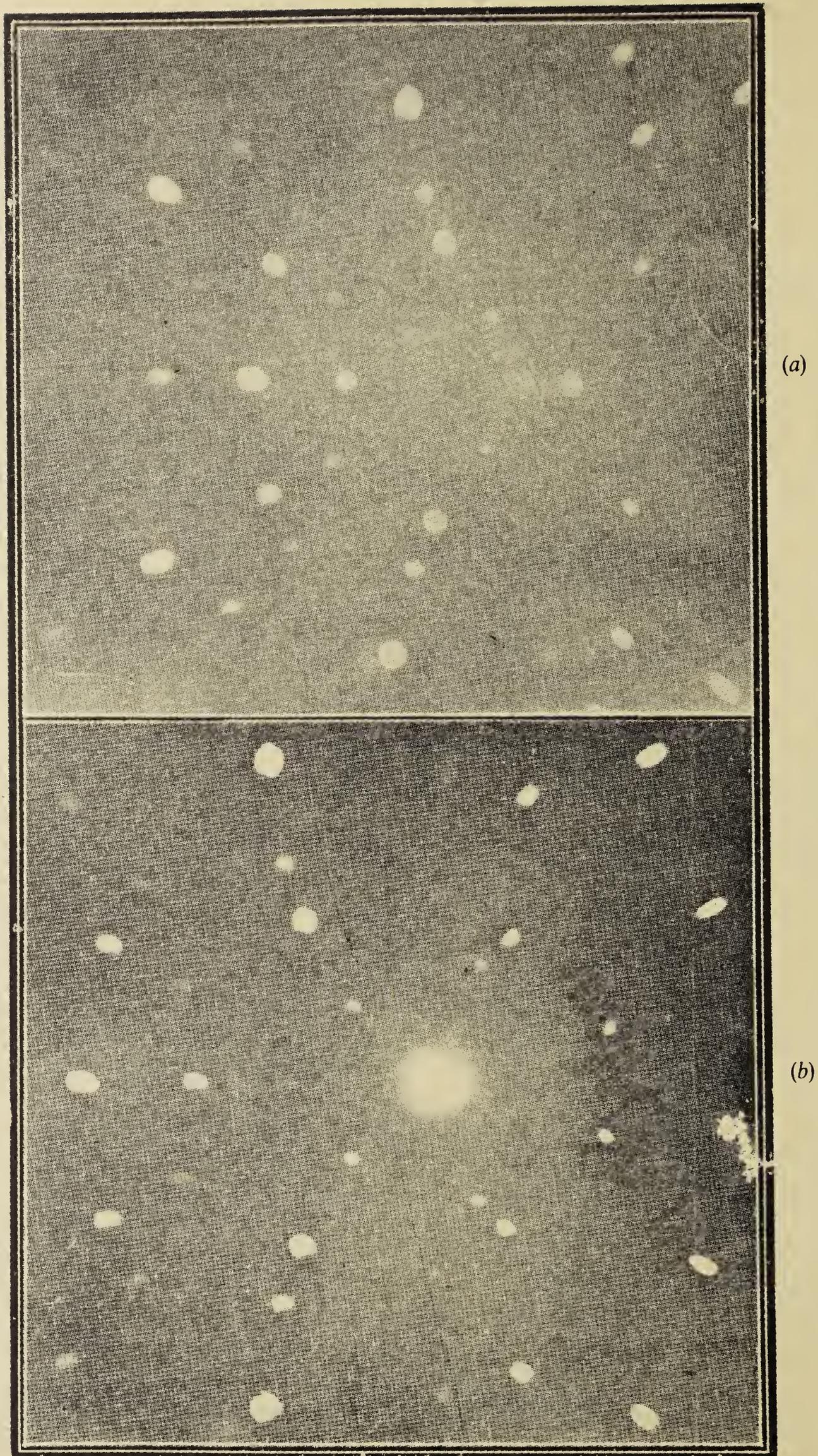


Figure 1. Laue patterns of octahedral diamond showing intense reflection by the (111) planes at different settings.

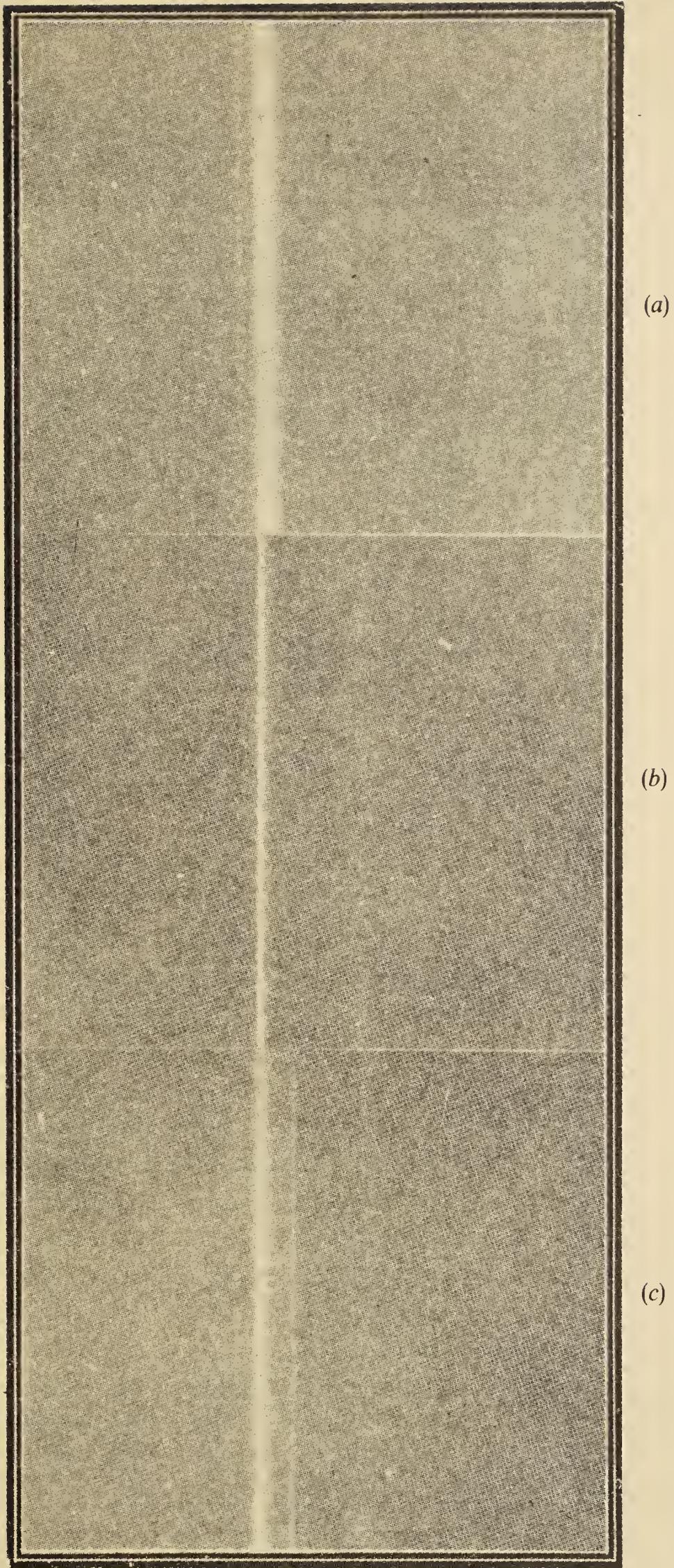


Figure 1. For explanation, see text.

Plate X

The infra-red absorption by diamond and its significance—Part I. Materials and methods

SIR C V RAMAN

Memoir No. 129 of the Raman Research Institute, Bangalore-6

Received November 11, 1961

1. Introduction

Diamond is a material of extraordinary interest and importance. Both by reason of the simplicity of its structure and composition and by reason of the variety of techniques available for the investigation of its spectroscopic behaviour, the study of diamond offers a most promising approach to the elucidation of the fundamental aspects of crystal physics. Questions such as the following need an answer. What is the nature of the atomic vibration spectrum of a crystalline solid and how is it related to its structure? Why does the passage of light through a crystal result in its diffusion with a change of frequency? In what circumstances and in what manner does the absorption of infra-red radiation occur in its passage through a crystal? How are the spectroscopic properties of a crystal related to its thermal energy content? Answers to these and many other questions are furnished by the facts which emerge from a study of the spectroscopic behaviour of diamond.

A remarkable property of diamond is that even selected material of the highest quality shows an astonishing variation of behaviour in certain respects, including especially its transparency to ultra-violet light and to infra-red radiation. Specially noteworthy also are the enormous variations observed in the intensity and spectral character of the visible luminescence exhibited by diamond under ultra-violet illumination. The explanation of these and other variations and the correlations which exist between them is an important part of the field of research presented by diamond and adds greatly to the interest of the subject. But in recognising this, one should not overlook the importance of finding answers to the fundamental questions which arise in respect of all diamonds. Indeed, not unless the more general questions have been satisfactorily answered can we hope to give the correct replies to the question why particular diamonds differ amongst themselves.

The morphology, structure and properties of diamond have interested the writer and have been the subject of numerous investigations and published

reports by him and his collaborators in earlier years. To enable these studies to be undertaken, specimens were acquired from time to time and the collection thus built up now includes some hundreds of diamonds of varied origins and of diverse forms and qualities. Crystals of diamond in their natural forms as found near Panna in Central India and from the South African mines form the most attractive items in the collection. But by far the most useful specimens included in the collection are the flat polished plates, one hundred in number, which are of diverse thicknesses and sizes and exhibit varied types of behaviour. There is no more convenient form of diamond for examining its optical properties than a flat polished plate, especially if its faces have a known crystallographic orientation, as is frequently the case for the plates in the writer's collection. It is obvious that for a real understanding of the problems presented by diamond, it is necessary to study such an extensive range of material and to examine the individual diamonds in detail in respect of diverse properties, and then to compare and correlate the results thus obtained. One of the most surprising facts about diamond is the existence of the correlations which come into evidence in an extremely striking and convincing fashion in such studies. That they must be recognised and need to be explained is obvious. But more important still is the fact that they point the way to a real understanding of the nature and properties of diamond.

2. Methods of study

It had long been the desire of the writer personally to study the infra-red behaviour of the entire collection of plates of diamond in his collection. But only recently however has the acquisition for this Institute of a Leitz recording infra-red spectrophotometer provided with both NaCl and KBr optics enabled this project to be seriously undertaken. The region of wavelengths between $1\ \mu$ and $15\ \mu$ can be traversed with the NaCl optics and between $13\ \mu$ and $24\ \mu$ with the KBr optics. With the spectrograph properly adjusted and worked, it becomes almost a routine operation to record the percentage transmission curves in these ranges. A special point of importance which has to be attended to is the most appropriate speed of operation. To get out the records quickly, one might be tempted to tend to run the spectrograph at the maximum permissible speed. But experience shows that, especially with the plates of smaller area, this is an erroneous procedure to follow. The best records are those in which the recording apparatus is set at slow speed as the maximum of detail and the highest definition are then obtained. Merely to record the percentage transmission curves of a large number of plates can serve no useful purpose unless one also examines each individual plate by other methods of study which can throw some light on the nature of the material under investigation. Of such methods there are several. But we shall here mention only three techniques which involve the minimum of

labour and at the same time are highly revealing. The first is the examination of the transparency of the material in the ultra-violet region of the spectrum. The second is the absence or presence of birefringence. The third is the visible luminescence of the diamond under ultra-violet illumination and especially the variations of the intensity and the colour of such luminescence.

A simple method of examination for ultra-violet transparency is to place the plate of diamond on a sheet of uranium-tinted glass which fluoresces strongly under ultra-violet illumination. A convenient source of such illumination is that commonly used for examining the luminescence of minerals, viz., a mercury vapour lamp in a tube of fused quartz, enclosed in a metal case one side of which is open but is covered by a filter which cuts off the visible light but allows the ultra-violet radiation of the lamp to pass through. When the lamp is held over the diamond, its transparency or lack of transparency is immediately revealed by the appearance presented by the glass plate as viewed either from above or from below. The area covered by the diamond appears dark if it is opaque and bright if it is transparent. While this simple technique suffices for a qualitative examination of the ultra-violet transparency of diamond, it is desirable to use the λ 2536.5 resonance radiation of the mercury arc isolated by a quartz monochromator for more critical studies in which it is sought to observe and photograph the variations, if any, which the plate of diamond exhibits in respect of its ultraviolet transparency over its entire area. We shall in a later part of this memoir return to the results obtained in this manner.

Examination of a diamond plate for the presence or absence of birefringence is a very simple matter. The diamond is placed on a strain-free glass plate and viewed through a pair of crossed polaroid sheets against a brilliant source of white light. Even the faintest birefringence becomes visible in these circumstances. The nature and character of the birefringence, if any, that is present can be determined by examination through a magnifier of appropriately chosen power.

The technique for observing the luminescence of the diamond is equally simple. The plate of diamond is placed on a sheet of black glass and a beam of sunlight filtered through a sheet of black glass which transmits only the ultra-violet part of the solar spectrum is focussed on it. The presence or absence of luminescence and its colour and intensity, if present, then become evident to observation. The use of filtered sunlight in the experiment ensures that the illumination of the diamond is of adequate intensity, so that a feeble luminescence is not mistakenly regarded as indicating the absence of luminescence. It is by no means generally the case that luminescence when present has the same intensity or colour over the entire area of the plate. It is possible, of course, to record the luminescence patterns of the diamond in such cases photographically on a colour film. It is sufficient, however, to photograph the luminescent diamond on ordinary film through appropriately chosen colour filters so as to exhibit these variations. We shall return in a later part of the memoir to this aspect of the subject.

3. Summary

The author's collection of diamonds includes one hundred polished plates of diverse thicknesses and sizes and exhibiting a varied behaviour. This form of diamond is exceptionally well suited for critical studies of the optical properties of diamond. The importance in the study and interpretation of the infra-red absorption by diamond of a parallel investigation of other properties is indicated. Of particular importance are three of them, viz., ultra-violet transparency, birefringence and luminescence. Simple and convenient methods for studying them are described.

The infra-red absorption by diamond and its significance—Part II. A general survey of the results

SIR C V RAMAN

Memoir No. 129 of the Raman Research Institute, Bangalore-6

Received November 28, 1961

1. Introduction

We now proceed to indicate in broad outline the results which have emerged from the investigations envisaged in the first part of this memoir. The outstanding facts of the subject will be stated and illustrated in an appropriate manner.

A critical examination of the optical behaviour of all the one hundred polished plates of diamond in the writer's collection reveals that they fall into three groups. Two groups of diamonds which we shall designate here as group A and group B each form about ten per cent of the entire number of specimens. The remaining eighty per cent of the diamonds will here be designated as group C. The diamonds in group A exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. The diamonds in group B also exhibit certain physical properties which are common to all of them and which distinguish them from all the other diamonds in the collection. But the properties of the diamond in group A and the properties of the diamond in group B are so strikingly contrasted that the observer is obliged to infer that they represent fundamentally different forms of diamond. That this is actually the case and that the crystal structures of the diamonds in group A and group B are indeed dissimilar, is demonstrated by the characters exhibited by the infra-red absorption spectra of the two groups of diamond. Their spectral behaviours are completely identical in some respects and completely dissimilar in other respects. Considered in conjunction with the other differences alluded to, it is clear that the facts admit of no explanation other than that we are here concerned with basic differences in crystal architecture. What these differences are is indicated in an unmistakable fashion by the spectroscopic observations.

The remaining eighty per cent of the diamonds which we have classed together as group C are shown by the studies to be *composite diamonds*, in other words, diamonds in which the structures characteristic of group A and the structures characteristic of group B are present side by side in the same specimen in juxtaposition. This is not an inference from theory but is a statement of actual

facts of observation. The geometric patterns of various sorts which these composite diamonds exhibit are visual evidences that over the area of any one cleavage plate of diamond, there are some parts which exhibit the characteristic properties of the diamonds of group A while the other parts exhibit the characteristic properties of diamonds of group B. Moreover, these parts are distributed over the area in regular crystallographic patterns which by themselves conclusively demonstrate that the diamonds of group A and the diamonds of group B are distinct crystallographic entities different from each other.

2. The physical behaviour of group A and group B diamonds

Ten diamonds of group A in the writer's collection and eight diamonds of group B have been set side by side and examined under identical conditions. The photographs of the two groups of diamond reproduced and exhibited alongside of each other in plate I were recorded simultaneously and with identical exposures and hence are strictly comparable with each other. The infra-red transmission curves of the largest diamond in group A and of the largest diamond in group B were also recorded in the NaCl range of the Leitz infra-red recording spectrophotometer and are reproduced respectively as figures 1 and 2 in the text below.

Turning to the photographs reproduced in plate I, we remark that the two pictures marked (a) and (a) respectively on its left and right sides exhibit the appearance of diamonds belonging respectively to the two groups as viewed between crossed polaroids against a bright white source of light. While the edges of the ten diamonds of group A are visible by reason of the light refracted at their

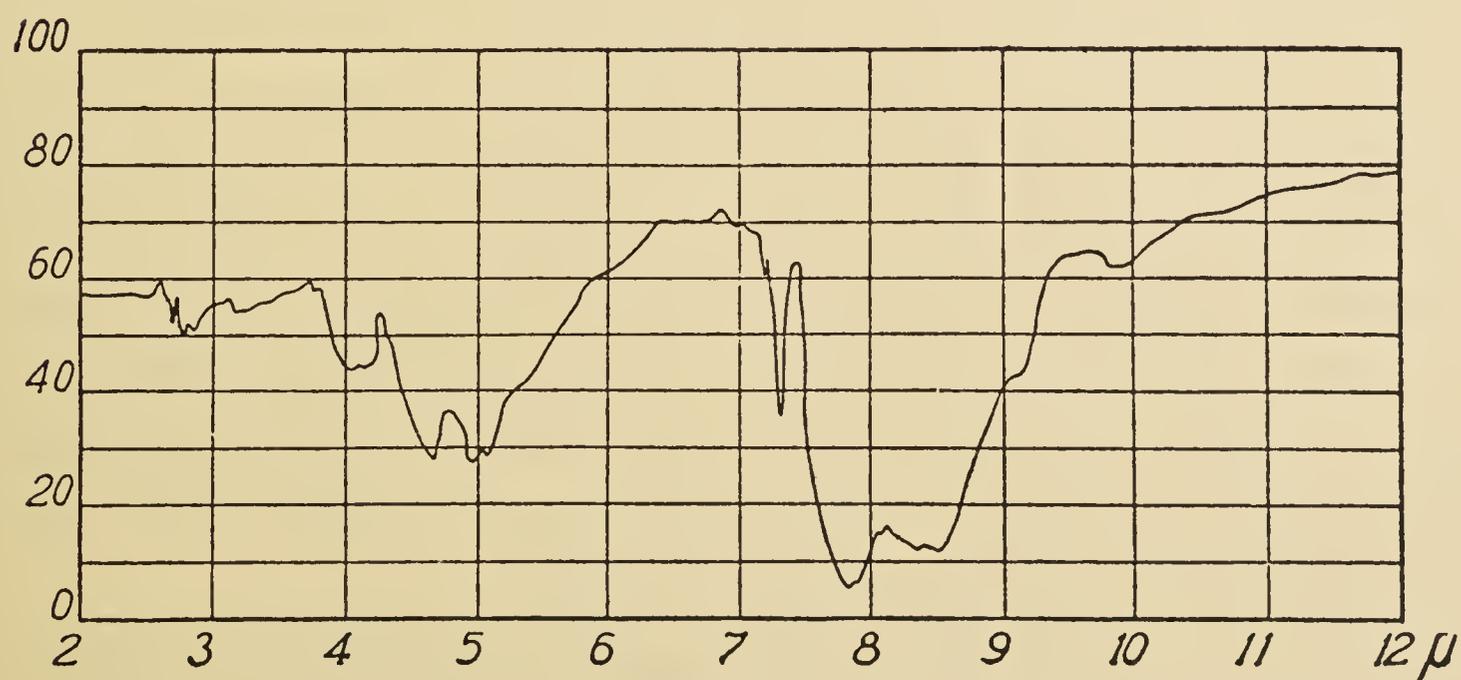


Figure 1. Infra-red transmission of group A diamond (thickness 1.01 mm).

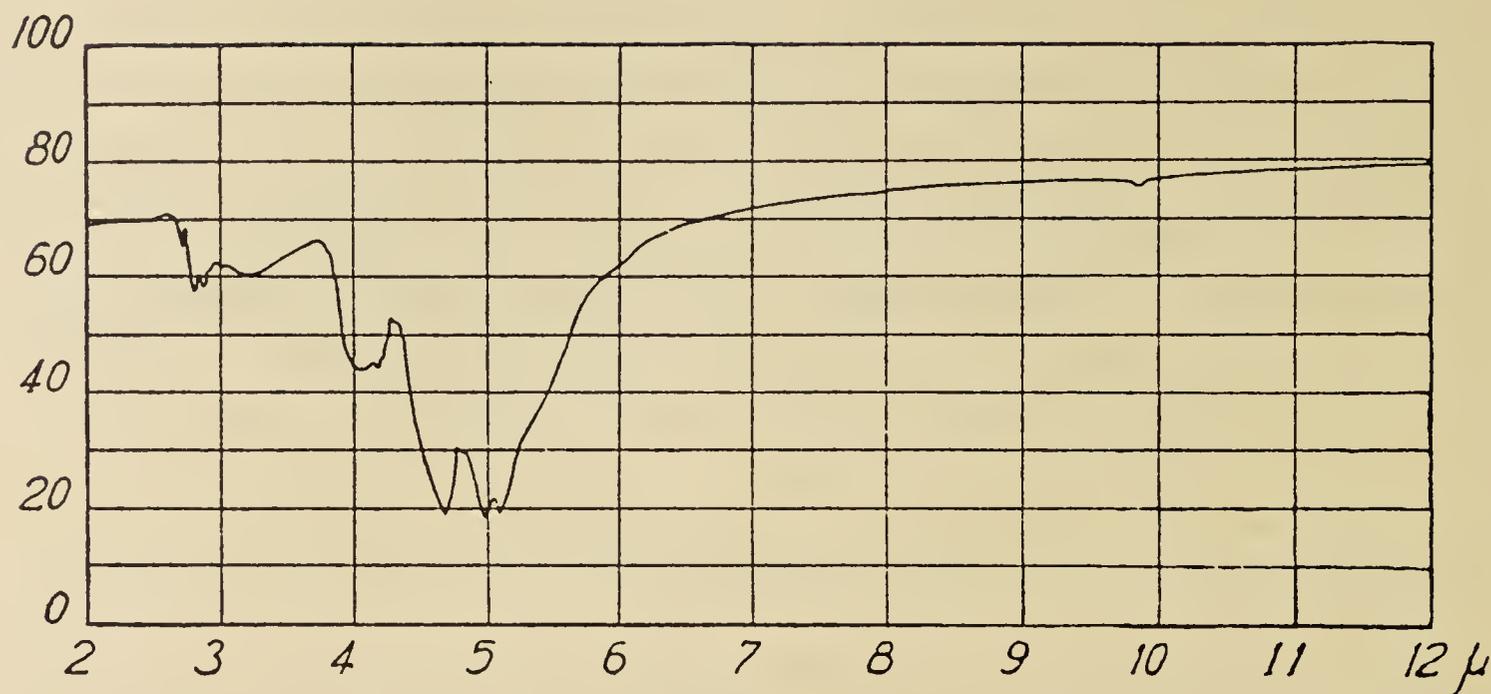


Figure 2. Infra-red transmission of group B diamond (thickness 1.06 mm).

peripheries, the plates themselves appear quite dark. In other words, the diamonds of group A are non-birefringent, and may hence be described as *truly isotropic and optically perfect diamonds*. On the other hand, all the eight diamonds of group B exhibit a marked restoration of light as seen between crossed polaroids. The patterns of birefringence which they exhibit differ from diamond to diamond both in respect of intensity and their geometric configuration, but in none of the eight specimens is the birefringence absent. Thus, we are justified in stating that the exhibition of a visible birefringence is a general characteristic of the diamonds of group B. We shall revert later to a more detailed consideration of the specific features of such birefringence.

The same ten diamonds of group A and eight diamonds of group B were examined for their transparency in the near ultraviolet region of the spectrum by the methods already described and explained in the first part of this memoir. They were placed on sheets of uranium-tinted glass and their transparency or opacity (as the case may be) in the near ultra-violet region of the spectrum stands immediately revealed by the luminosity of those sheets, as is seen from the photographs reproduced in plate I and marked (b) and (b) respectively on the left and right of the pictures. It will be seen that all the diamonds of group A exhibit complete opacity, while those of group B are highly transparent to the part of the spectrum under consideration. As between themselves, the eight diamonds of group B exhibit some differences in respect of their transparency. These differences are ascribable to a slight yellowish tinge exhibited by some of the specimens, while the others are perfectly colourless.

Finally, the photographs reproduced in plate I and marked (c) and (c) respectively on the left and the right exhibit the behaviour of the same ten diamonds of group A and the same eight diamonds of group B in respect of the

luminescence excited by the incidence of ultra-violet radiation. The two groups of diamond were placed side by side on a sheet of ordinary glass and strongly illuminated by the light of three mercury lamps enclosed in Wood's glass which cut out all the visible light except some deep red. The glass sheet with the diamonds adherent to it was photographed through a cell containing an aqueous solution of sodium nitrite. This filter cuts off the scattered or reflected ultra-violet light and allows only the visible luminescence to come through. It will be seen from the plate that all the diamonds of group A exhibit a visible luminescence but with very different intensities in the different diamonds. The colour of the luminescence as actually observed was a clear blue in all cases. On the other hand, all the diamonds of group B are seen to be definitely non-luminescent.

We may sum up the information exhibited by plate I as follows: The diamonds of group A are isotropic and optically perfect diamonds. They are opaque to ultra-violet radiation less than 0.3μ in wavelength, and exhibit a visible blue luminescence under ultra-violet irradiation but of varying degrees of intensity. On the other hand, the diamonds of group B exhibit a readily observable birefringence, are transparent to ultra-violet radiation of wavelengths between 0.3μ and 0.25μ , and are non-luminescent. These properties of the two groups of diamond go hand in hand with the differences in the behaviour towards infra-red radiation exhibited in figures 1 and 2 in the text above. A detailed discussion of the features noticed in these spectrographic records will appear in later parts of this memoir. It will suffice here to draw attention to some of their outstanding features. The thickness of the group B diamond whose record is reproduced in figure 2 is distinctly greater than that of the group A diamond whose record is reproduced in figure 1. Due allowance being made for the effect of the greater thickness on the percentage transmission curves, it will be seen that in the spectral region between 2μ and 6μ , the two diamonds exhibit features which are indistinguishable from each other. On the other hand between 6μ and 12μ , the behaviour of the two diamonds is totally dissimilar. The group A diamond exhibits an absorption which goes up steeply beyond 7μ and a whole series of absorption maxima appear thereafter, while on the other hand, the group B diamond is highly transparent throughout this range. Any attempt to explain these facts should necessarily take into account the facts revealed by the photographs reproduced in plate I and should be based on sound physical reasoning and not on *ad hoc* suppositions of the kind which one finds frequently in the literature and which can only be described as completely irrational.

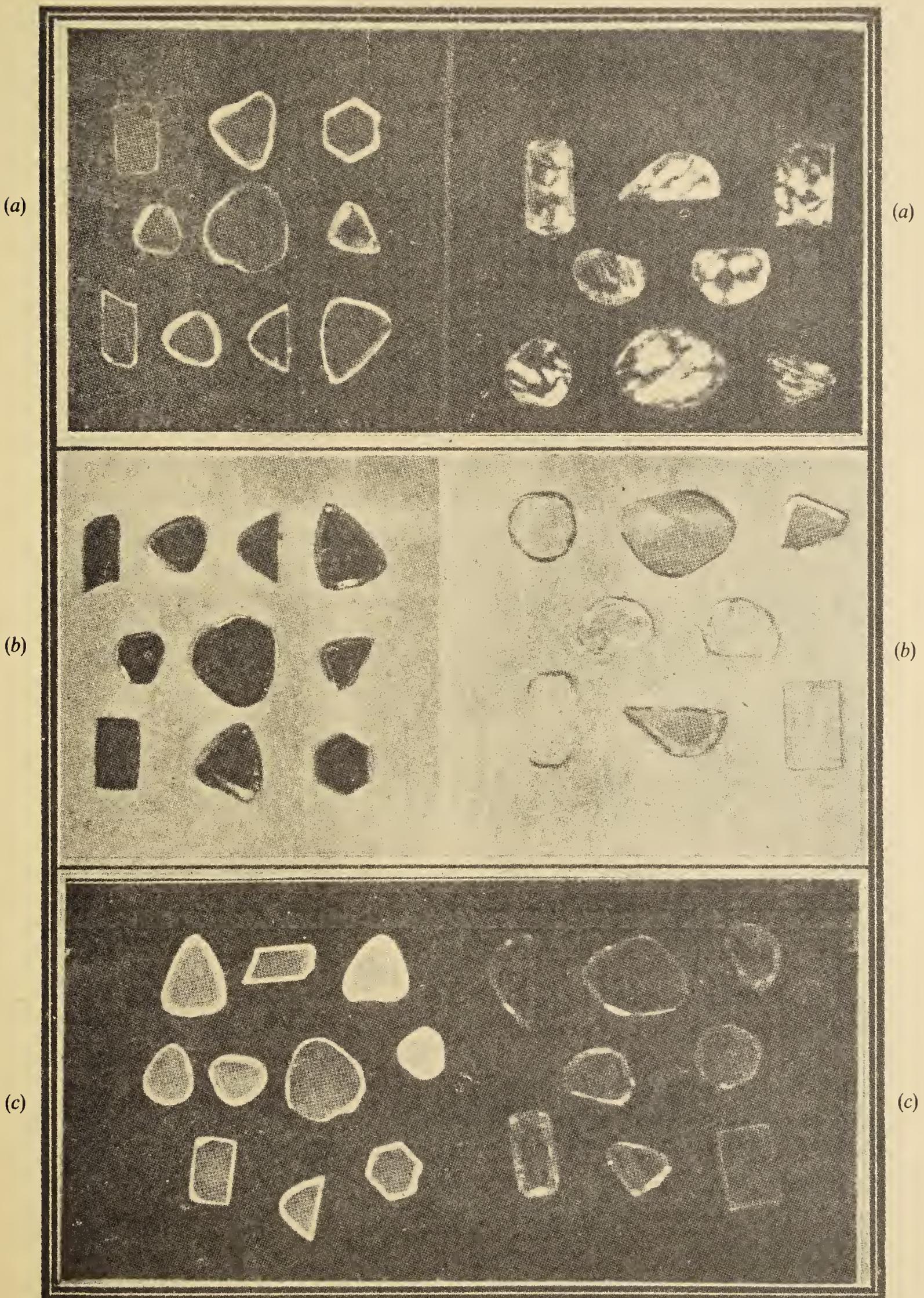
3. Summary

Approximately ten per cent of the total number of diamonds form group A and another ten per cent group B. These two groups exhibit highly contrasting characters. Group A diamonds are isotropic and optically perfect, are opaque to

ultra-violet of wavelengths less than 0.3μ and exhibit a visible blue luminescence. Group B diamonds are visibly birefringent, their transparency extends well beyond 0.3μ and they are non-luminescent. The two groups differ strikingly in their infra-red behaviour. These facts taken in conjunction indicate that the two groups of diamond differ fundamentally in their crystal structure.

Group A

Group B



Ten diamonds of Group A and eight of Group B examined under similar conditions.

The infra-red absorption by diamond and its significance—Part III. The perfect diamonds and their spectral behaviour

SIR C V RAMAN

Memoir No. 129 of the Raman Research Institute, Bangalore-6

Received December 6, 1961

1. Introduction

A perfect diamond should be colourless and transparent and should be free from internal cracks and inclusions and should further exhibit no visible birefringence when placed between crossed polaroids and viewed against a bright source of light. This last test is a stringent one and it serves to exclude a large majority of diamonds. The specimens that do satisfy the test also exhibit the other properties characteristic of the group A diamonds described and illustrated in the second part of this memoir. We shall in the present part deal a little more fully with their optical characters and especially with their infra-red behaviour.

A fine example of a perfect diamond is the tabular crystal in its natural hexagonal form which was presented to the author by the late Dr Paul Grodzinski. Photographs of this diamond obtained by four different techniques are reproduced in plate I. The picture marked (*a*) was obtained with the diamond placed on a fluorescent plate and illumined by the λ 2536.5 radiations of a mercury arc which traversed the diamond before reaching the plate. The photograph exhibits the opacity of the diamond to the radiations. The photographs marked (*b*) was obtained with the diamond held between crossed polaroids and exhibits its perfect freedom from birefringence. The photographs marked (*c*) and (*d*) were obtained with the diamond illumined by sunlight filtered through a plate of Wood's glass. Photograph (*c*) exhibits the faint blue luminescence of the diamond as seen through a filter of blue glass. The exposure was so prolonged that the luminescence was recorded with great intensity. Photograph (*d*) represents the luminescent diamond in the same circumstances as viewed through a filter of yellow glass. It will be noticed that the luminescence is then unobservable.

The photographs reproduced in plate II and marked (*a*), (*b*), (*c*) and (*d*) were obtained using similar procedures with a cleavage plate of diamond of Indian

origin. It will be noticed that the effects exhibited by it are in each case similar to those seen in plate I.

2. Characteristic features of the absorption

In the first part of this memoir, reference was made to the desirability of recording the transmission curves with the Leitz instrument at a very low speed. The importance of this remark is illustrated by figure 1 in the text below which is the record in the $2\mu - 12\mu$ region obtained with a perfect diamond 0.81 mm thick, the speed of recording being at the rate of 10 minutes per μ of wavelength. A comparison with the record of another diamond of the same class but recorded at a speed of 3 minutes per μ and reproduced as figure 1 in the second part of this memoir shows that the slower speed greatly improves the sharpness and precision of the recording. This is especially evident in the region of wavelengths between 7μ and 10μ where the features exhibited by the perfect diamonds make their appearance and which we shall now proceed to discuss.

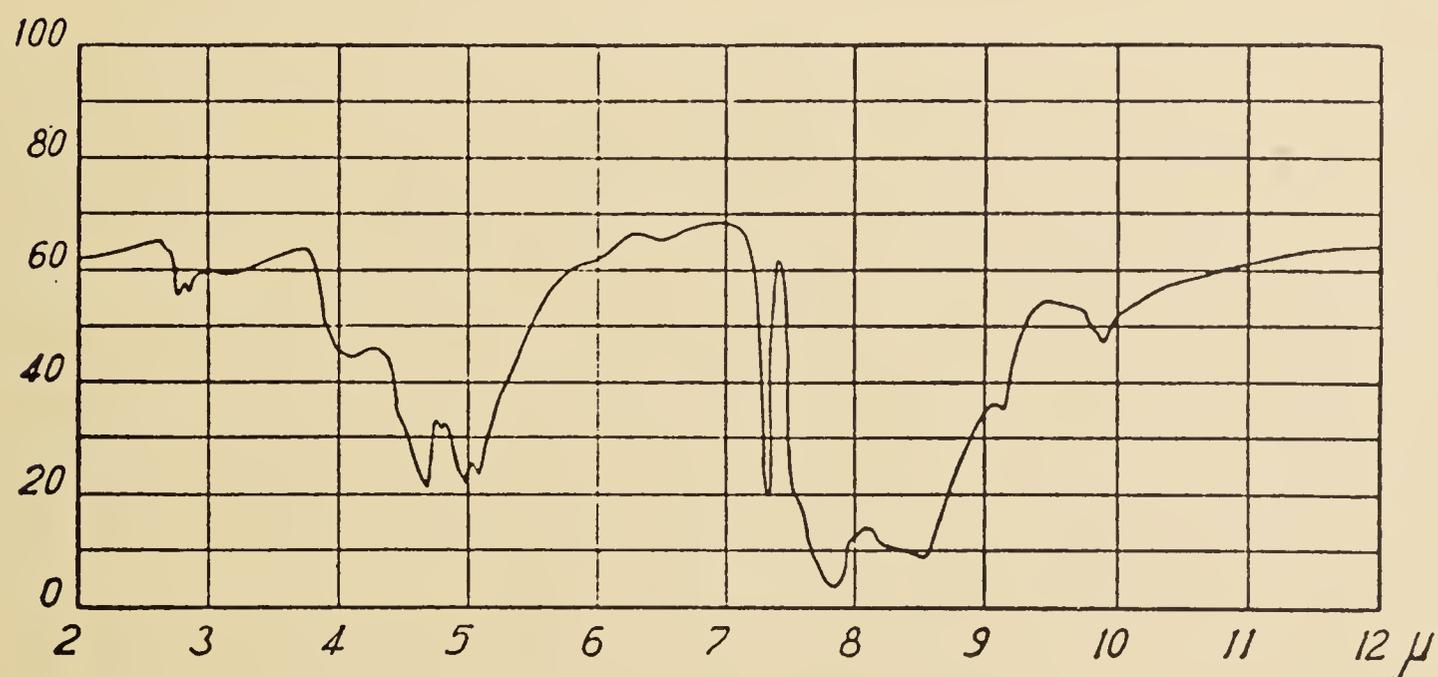


Figure 1. Percentage transmission curve of a perfect diamond (thickness 0.81 mm).

A very remarkable feature of the absorption spectra of the perfect diamonds is the sudden increase in absorption which appears between 7.4μ and 7.5μ . This is very clearly shown in figure 1, the transmission falling from 62 to 20% within a range of only 0.1μ . The curve coincides with the 7.5μ ordinate in the region where the transmission falls from 40 to 20% and then suddenly alters its course. The sharp absorption edge at 7.5μ (or in wave-numbers 1332 cm^{-1}) is thus a highly characteristic feature exhibited by the perfect diamonds. It is well known that in the spectrum of the scattering of light by diamond, a sharply defined frequency shift of 1332 cm^{-1} is recorded. This quantitative agreement in respect of

frequency makes it evident that in both cases we are concerned with effects arising out of the structure of diamond itself.

Besides the edge at 7.5μ , the record reproduced as figure 1 shows other well-marked features at longer wavelengths, viz., an absolute minimum of transmission at 7.85μ , a sharp turn in the course of the record at 8.2μ , another very sharp turn at 8.5μ , another turn followed by a very steep rise at 9.2μ and finally a well-defined peak at 9.9μ . Diamond thus exhibits in its absorption spectrum in this range six clearly defined features at 7.5μ , 7.85μ , 8.2μ , 8.5μ , 9.2μ and 9.9μ respectively. Expressed as frequencies in wave-numbers, these are at 1332, 1273, 1219, 1176, 1087 and 1010 cm^{-1} respectively. The appearance of these features in infra-red absorption would be accounted for if the crystal structure had specific vibrational modes having the frequencies listed and the radiations traversing diamonds of this class excited such vibrations. In other words, the region of wavelengths between 7.5μ and 10μ exhibits the infra-red absorption spectrum of the first order of the perfect diamonds.

3. The absorption spectra of higher orders

Since, as we have seen, the first-order absorption spectrum commences at 1332 cm^{-1} and extends towards lower frequencies, the second-order spectrum exhibiting the first overtones of the fundamental frequencies should commence at 2664 cm^{-1} and extend towards lower frequencies. Likewise, the third-order spectrum should commence at 3996 cm^{-1} and continue to lower frequencies. The same limits expressed as wavelengths are 7.5μ , 3.75μ and 2.5μ respectively. Actually, it is seen from figure 1 above that there is a large and sudden drop in the percentage transmission at about 3.75μ and another but less conspicuous drop in transmission at about 2.6μ . It is thus evident that the perfect diamonds exhibit the complete absorption spectrum including the first, second and third orders at the appropriate wavelengths and frequencies.

We may here draw attention to the most conspicuous features in the second-order spectrum, viz., the extremely sharp minimum of transmission at 4.60μ or 2174 cm^{-1} , the double peak at 4.95μ and 5.09μ or 2020 cm^{-1} and 1965 cm^{-1} . We may also draw attention to the sudden fall in transmission from 68% at 7μ to 21% at 7.30μ followed by an equally sudden rise to 62% at 7.40μ . This very remarkable feature in the second-order spectrum evidently stands in a close physical relationship to the sharp absorption edge at 7.5μ appearing in the first-order spectrum, as is shown by the fact that it does not appear in the case of group B diamonds which show only the second and third-order spectra, and not that of the first order. As will be explained in a subsequent part of this memoir, the sharp dip at 7.30μ or 1370 cm^{-1} is the result of the excitation of a summation of the two lowest, viz., the seventh and eighth vibrational frequencies of the diamond structure which are at 746 cm^{-1} and 624 cm^{-1} respectively (13.40μ and 16.02μ

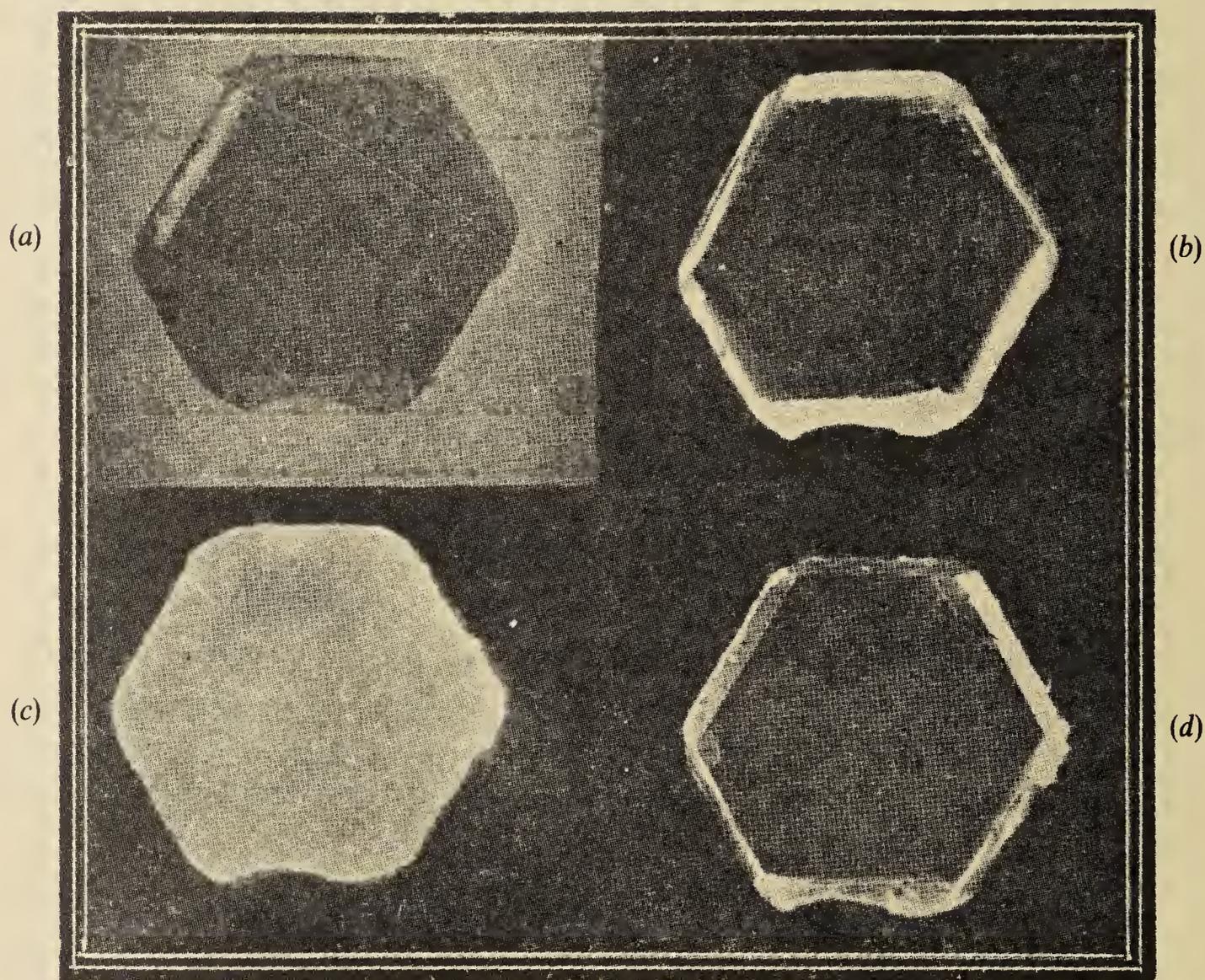
when expressed as wavelengths). The summational frequency is powerfully excited in absorption by reason of its close contiguity to the principal 1332 cm^{-1} frequency which is active in the perfect diamonds.

It may also be remarked that the sharp peaks at 2174 cm^{-1} and 2020 cm^{-1} are the octaves of the fifth and sixth vibrational frequencies of diamond which, as we have already noticed, manifest themselves clearly as fundamentals in its first-order absorption spectrum. The third sharply defined peak at 1965 cm^{-1} results from a summation of two fundamental frequencies of vibration, viz., 1219 cm^{-1} and 746 cm^{-1} respectively.

The various sharply defined features observed in the second-order absorption of diamond are thus a clear demonstration that the *atomic nuclei in the structure of diamond possess a set of free vibrational modes with discrete monochromatic frequencies*. On the other hand, the infra-red absorption spectrum represents the *forced vibrations* of the structure produced by the field of the incident radiation acting on the electrons which hold the nuclei in place. It is necessarily recorded as a continuous curve exhibiting peaks or sharp turns or sudden drops at positions determined by the nuclear vibration frequencies.

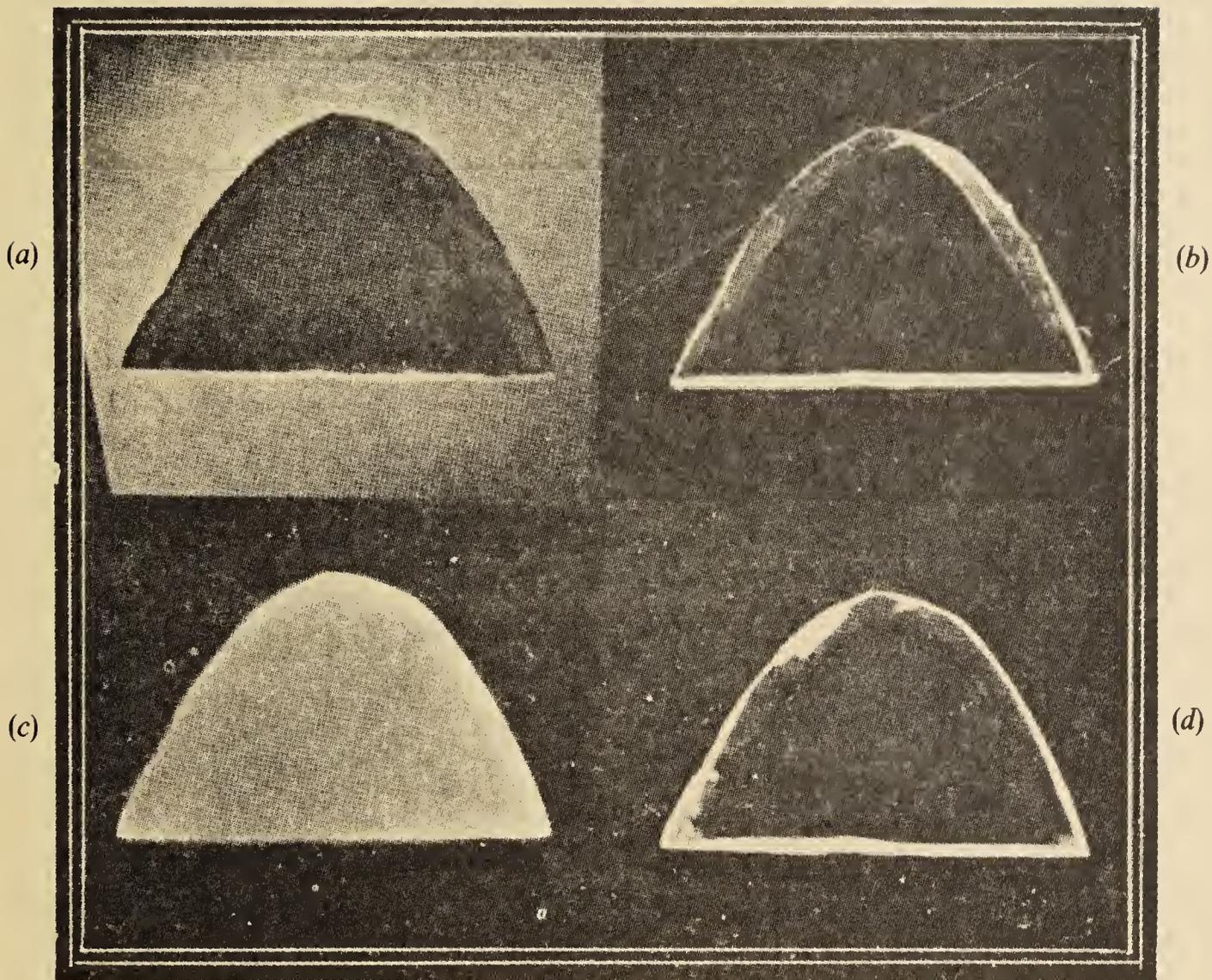
4. Summary

The perfect diamonds exhibit an absorption which is readily recognised as including the first, second and third order spectra. From the features observed in these spectra it is inferred that the diamond structure has eight discrete frequencies of free vibration, viz., 1332 , 1273 , 1219 , 1176 , 1087 , 1010 , 746 and 624 cm^{-1} . The fifth and the sixth frequencies appear very prominently with doubled frequency as sharp peaks in the second-order absorption spectrum, while a summation of the seventh and eighth frequencies is recorded with extraordinary strength and sharpness by reason of its contiguity to the active fundamental of highest frequency.



A perfect diamond (tabular crystal).

Plate I



A perfect diamond (cleavage plate).

Plate II

The infra-red absorption by diamond and its significance—Part IV. The non-luminescent diamonds

SIR C V RAMAN

Memoir No. 129 of the Raman Research Institute, Bangalore-6

Received December 9, 1961

1. Introduction

The special properties which distinguish group B diamonds from the group A or perfect diamonds have already been described and illustrated in the second part of this memoir. Photographs of individual diamonds of the group B class on a somewhat larger scale are however needed to exhibit these properties in an adequate fashion. Accordingly, enlarged pictures of two of these diamonds have been reproduced in plate I. Both of these diamonds are polished plates. While the semicircular diamond has rough edges, the other is a diamond cut into a rectangular shape and its edges as well as its faces given a good polish.

The two photographs marked (a) and (a) in plate I exhibit a property characteristic of the group B diamonds, viz., their transparency to the λ 2536.5 radiations of the mercury arc. The radiations traversed the diamonds before reaching the fluorescent plate on which they were placed. The perfect transparency of the diamonds to the ultra-violet radiations is displayed by the fluorescence of the supporting plate in the areas covered by the diamond and the areas not so covered being of equal intensity. It may be remarked that the transparency of the diamonds of group B to the λ 2536.5 radiations is of great importance from a practical point of view. For, it enables these diamonds to be used for studies of the spectrum of light-scattering with the resonance radiation from a water-cooled magnet-controlled mercury arc as the exciter. The second-order spectrum of light-scattering in diamond can then be successfully recorded.

As has already been noted in the first part of this memoir, the group B diamonds present a striking contrast with group A or perfect diamonds in exhibiting a readily observable birefringence. This effect was illustrated in plate I accompanying the second part of this memoir, but the photographs were on much too small a scale to reveal the real nature of the phenomenon. The photographs now reproduced as (b) and (b) in plate I are on a larger scale. Crossing the irregular dark and bright areas can be glimpsed numerous parallel streaks of varying brightness. A still larger magnification is, however, needed fully

to exhibit the character of the birefringence. In plate II is reproduced an enlargement of the birefringence pattern of a plate of diamond 14 mm by 9 mm in size and 1.47 mm in thickness. On the same scale below it is reproduced a photograph exhibiting the ultra-violet transparency of the diamond. It may be remarked neither in plate I (b) and (b) nor in plate II (b) does the smallest trace of the structures so clearly seen in the birefringence pattern come into evidence in the ultra-violet transparency, though the latter was observed and photographed under conditions entirely favourable for exhibiting the variations of transparency over the area of the diamond, had they been present.

Finally, we may draw attention to the photographs of the two diamonds marked (c) and (c) in plate I. These exhibit the complete absence of any luminescence of these diamonds under ultra-violet illumination.

2. The infra-red absorption spectra

The transparency of the group B diamonds in the ultra-violet region of the spectrum around 0.25μ as contrasted with the opacity of the group A diamonds in the same region goes hand in hand with the absence in the group B diamonds of the characteristic absorption between 7μ and 10μ in the infra-red conspicuously exhibited by the group A diamonds. The relationships between the spectral behaviour of group A and of group B diamonds in the near ultra-violet and in the near infra-red are so clear and quantitatively so definite as to leave no doubt that the explanation in both cases has to be sought for on the same lines, viz., a fundamental difference in the structure of the diamonds in the two groups. We shall return to this subject later on and shall meanwhile describe and illustrate the infra-red behaviour of group B diamonds a little more fully than before.

Figure 1 below is the record of the percentage of transmission in the region between 2μ and 12μ of a non-luminescent diamond plate of thickness of 1.07 mm.

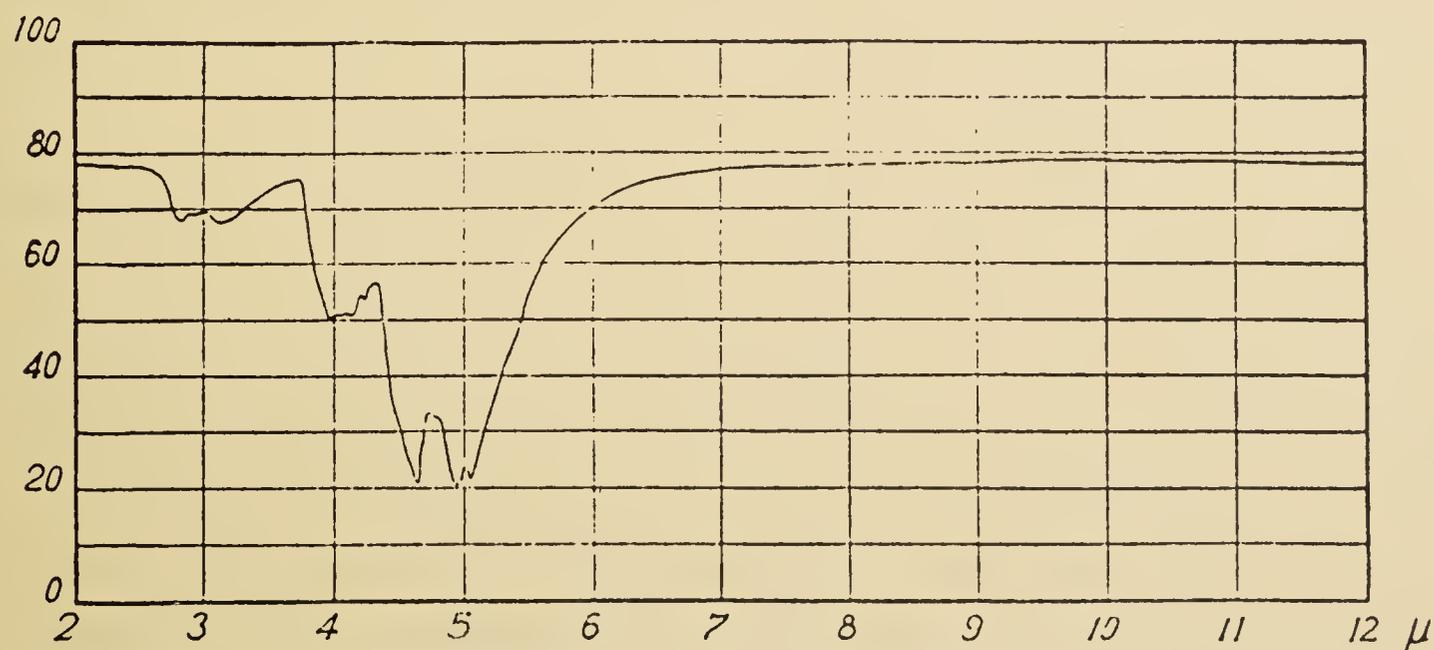


Figure 1. Transmission percentages of a non-luminescent diamond (thickness 1.07 mm).

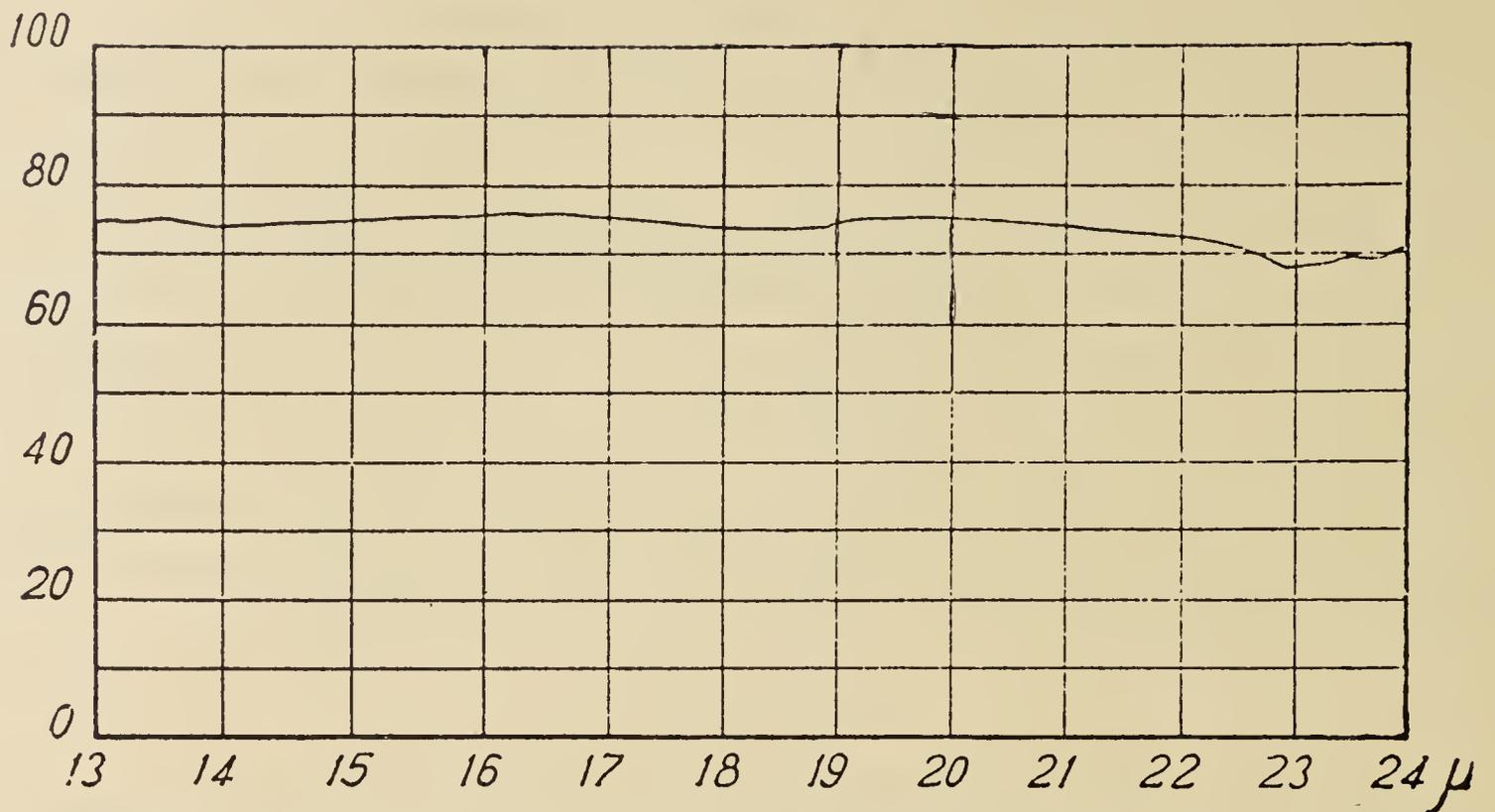


Figure 2. Transmission percentages of a non-luminescent diamond (thickness 1.07 mm).

Figure 2 is a record with the same plate for the region between 13μ and 24μ , and it will be noticed that this is practically featureless. From the two records taken together, it is evident that if we take into account the loss by reflection at the two faces of the plate, these diamonds exhibit a practically complete transparency over the entire wavelength range between 7μ and 24μ . On the other hand, between 2μ and 6μ , they exhibit a very marked absorption which may be identified with the second-order and third-order spectra of diamond, the first order being totally absent. We may compare these with the features noticed in the same region of wavelengths in figure 1 in the text of the third part of the memoir. That figure was the record of a perfect diamond showing all the three orders of absorption. In the region between 2μ and 6μ , the two figures are practically indistinguishable from each other. In particular, the sharply defined minima of transmission appear, within the limits of accuracy of the recording mechanism, at the same positions in both cases.

We may here remark that the features appearing in the second-order absorption spectra are very clearly related to the features in the first-order absorption recorded with the perfect diamonds. Some of these relationships have already been pointed out in the previous part of the memoir and we may here usefully draw attention to a few others. The steep fall in the transmission percentage which commences at 3.75μ and terminates at 4μ has its counterpart in the first-order absorption of the perfect diamonds which rises quickly and reaches its highest values in the wavelength range between 7.5μ and 8μ . The steep increase in absorption which commences at 4.3μ and culminates at the sharp minimum at 4.62μ in the second-order spectrum has its counterpart in the first-order in the steep increase in transmission which commences at 8.55μ and after a

brief arrest at 9.15μ continues again beyond that wavelength. Then again, the fall in absorption between the two sharp peaks located at 4.62μ and 4.95μ appearing in the second-order absorption has its counterpart in the first-order absorption in the increased transmission appearing in the region between 9.2μ and 9.9μ . These quantitative correspondences between the spectra of the two orders indicate that both spectra are based on the excitation of the same set of vibrational modes with discrete frequencies, though the activities of these modes in the first-order and the second-order may be altogether different. Indeed, it is clear from the facts that the fifth and sixth vibrational modes are those exhibiting the greatest infra-red activity in the second-order, whereas in the first-order absorption, when it is manifested, the first few modes are far more active than all the others.

3. Nature and origin of the birefringence

We may next proceed to describe and discuss the patterns of birefringence which the non-luminescent diamonds exhibit. To observe the patterns, it is a convenient procedure to place the diamond on a glass plate which can be rotated between two crossed polaroids and to view the specimen through a magnifier of suitably chosen power. As the plates of diamond are usually not very thick, it is possible to use a high-power lens and this is indeed necessary to obtain a correct idea of the characters of the birefringence.

All the diamonds of the non-luminescent class in the author's collection have been examined and their birefringence patterns have been found to exhibit certain general characteristics. The restoration of light which is observed is not uniform over the area of the diamond but is seen resolved into a series of parallel bands which are alternately dark and bright. These bands run continuously across the diamond from periphery to periphery. In nearly all the cases, one notices two sets of such bands cutting across each other, but they are not always equally prominent. As the diamond is rotated between the crossed polaroids, each set of bands disappears when it is parallel to the plane of polarisation of the polariser or of the analyser, and is seen most clearly when it bisects the angle between them. In the cases when the two sets of bands cut each other at right angles, they appear and disappear simultaneously as the diamond is rotated.

Examined under the higher magnifications, the bands in the pattern appear as bundles of fine thread-like lines of light. By reason of their criss-crossing, the pattern has a lace-like appearance. Due to the criss-crossing also, the threads exhibit a wavy outline and are not perfectly straight. Some idea of these effects can be gathered from the photographs reproduced in plates I and II accompanying this part of the memoir.

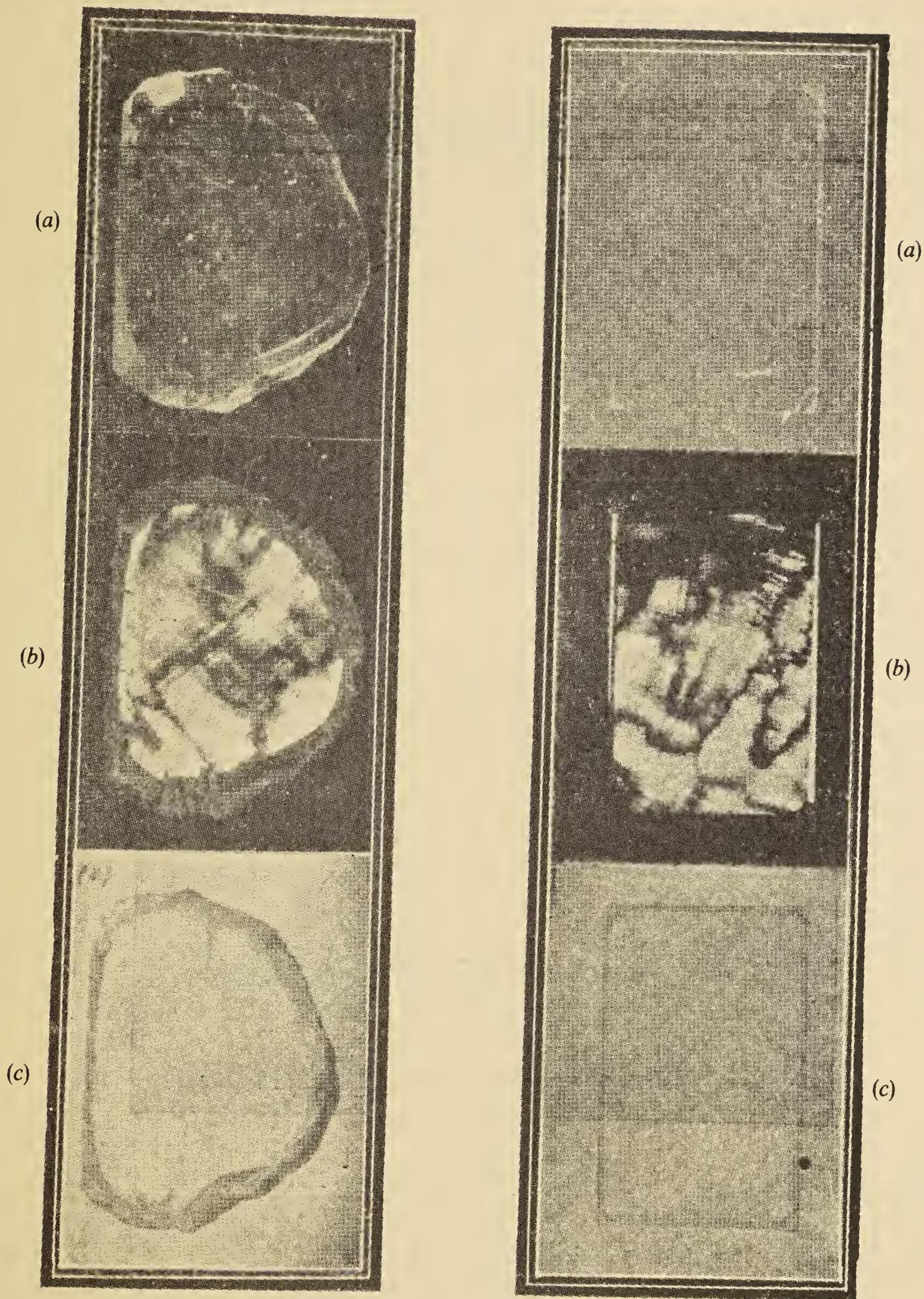
The mutual orientation of the two sets of bands and their alignment with respect to the crystal structure are obviously matters of importance. In some of the plates, they are seen to be mutually perpendicular, while in others they run at

an angle to each other which is approximately sixty degrees. To determine their crystallographic orientation, it is necessary to know the orientation of the plate of diamond in which they are seen. In this connection a reference should be made to the thorough and painstaking studies carried out by G N Ramachandran on the birefringence of diamonds (*Proc. Indian Acad. Sci.*, A24, 65, (1946)). Ramachandran's investigations covered not only the diamonds of the non-luminescent class but also the composite diamonds which will form the subject of the fifth part of this memoir. Using a petrographic microscope in conjunction with a Federov universal rotating stage, he discovered that the structural birefringence observed in diamond has its origin in the presence of laminations in the structure which are orientated parallel to the octahedral planes or to the dodecahedral planes of the crystal or to both. He also determined the magnitude of the birefringence in various cases. His observations with the non-luminescent diamonds were particularly significant. They showed clearly that the birefringence pattern exhibited by such plates when viewed normally between crossed polaroids arises from a lamellar structure of the kind referred to. Why such a lamellar structure is present in diamonds of this class associated with the various other properties described earlier is a question the answer to which is evidently to be found in the basic facts of the architecture of the diamond crystal.

4. Summary

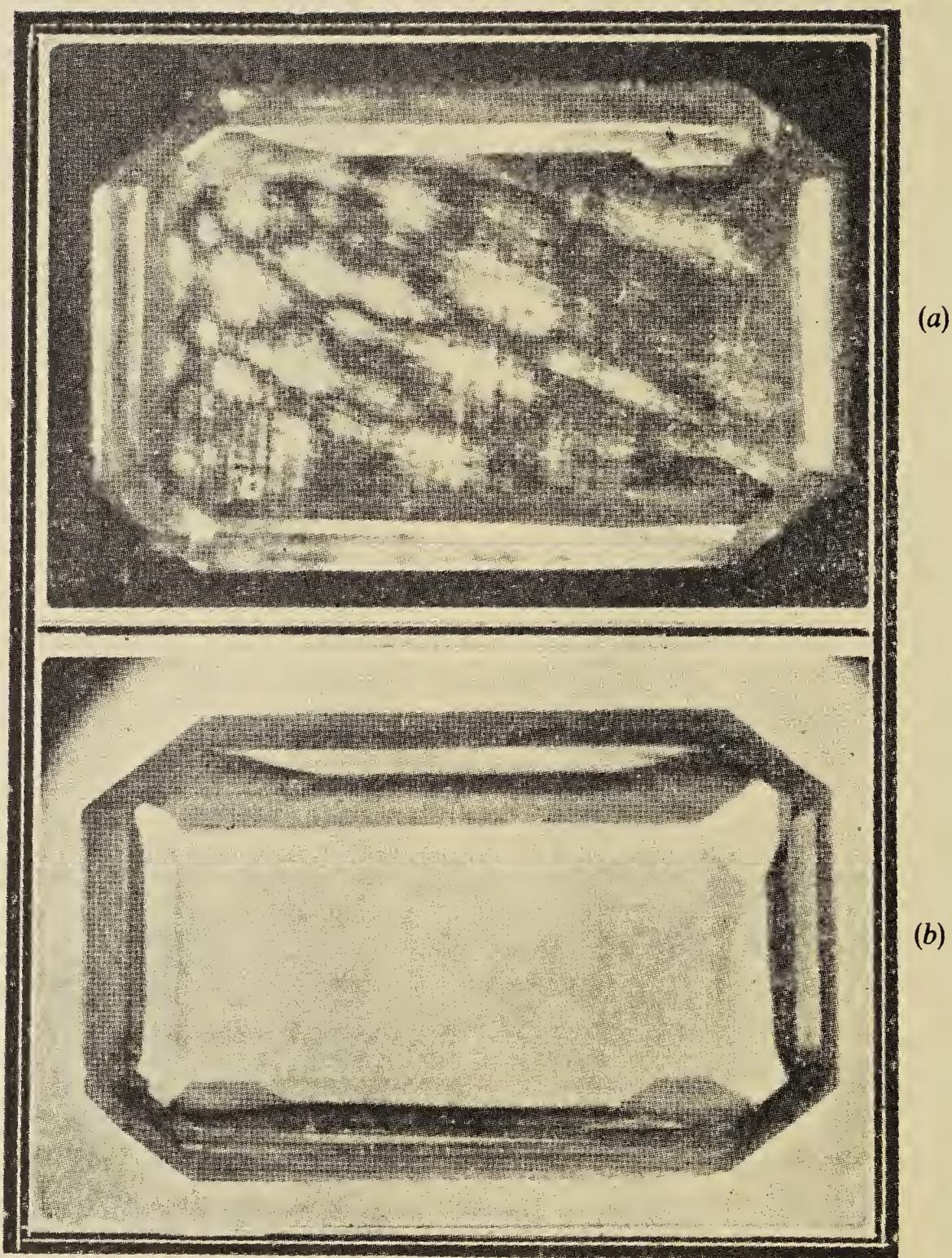
The non-luminescent diamonds exhibit the infra-red absorption spectra of the second- and third-orders, while the first-order is totally absent. A critical examination of the spectrographic records shows clearly that the second-order spectrum is based on the same vibrational modes with discrete frequencies as the first, the activities of the modes, however, being different in the two cases.

The non-luminescent diamonds exhibit a type of birefringence which arises from the presence in them of laminations orientated parallel to the octahedral planes or to the dodecahedral planes of the crystals or to both.



Two non-luminescent diamonds.

Plate I



(a) Birefringence and (b) ultra-violet transparency.

Plate II

The infra-red absorption by diamond and its significance—Part V. The composite diamonds

SIR C V RAMAN

Memoir No. 129 of the Raman Research Institute, Bangalore-6

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1. Introduction

The many striking differences in the physical behaviour of the perfect diamonds and of the non-luminescent diamonds are a sufficient demonstration that their crystal structures are fundamentally different. Nevertheless, their structures must be closely related to each other. For, they have infra-red absorption spectra which in the second and third orders are indistinguishable, while the first order is present only for the perfect diamonds and absent for the non-luminescent ones. Spectroscopic theory considered in the light of the mechanism of infra-red absorption gives us the clue to the origin of these differences. But the differences are evidently not of such a nature as to preclude the two structures appearing in juxtaposition in one and the same diamond. Indeed, this is so frequently the case that the composite diamonds, as we shall call them, form the large majority amongst the polished plates of diamond in the writer's collection. As has already been mentioned, about ten per cent of the specimens are perfect diamonds, another ten per cent are non-luminescent ones, while the remaining eighty per cent are composite diamonds.

2. Proofs of the composite nature

The easiest and also the most convincing demonstration that any particular specimen is a composite diamond is furnished by observations of its ultra-violet transparency. The technique of such observations has already been described. The λ 2536.5 radiation of a mercury arc lamp passes through the diamond and is then incident on a fluorescent plate in close contact with it. The luminescence of the plate then immediately reveals the variations in the transparency of the diamond over the different parts of its area.

Another very instructive demonstration of the composite nature of a diamond is furnished by observations of the luminescence excited by ultra-violet radiation.

Such luminescence may be observed either through a filter which transmits only the blue end of the spectrum or through a yellow filter which cuts out the blue and green altogether and transmits only the yellow, orange and red. The characters of the luminescence are found to be totally different as observed through the two filters and these differences are very revealing in respect of the structure of the diamond.

Still another method of observation is to view the diamond between crossed polaroids against a bright source of light. A perfect diamond would, of course, exhibit no birefringence. A non-luminescent diamond, on the other hand, would exhibit a birefringence of the kind described in the fourth part of this memoir, but no trace of the structure thus revealed would appear in its ultra-violet transparency. Composite diamonds, on the other hand, exhibit birefringence patterns of which the features can be recognised both in the ultra-violet transparency patterns and in the patterns of luminescence, and especially in the latter as seen through a yellow filter.

Seven polished plates of diamond in the writer's collection have been photographed by each of the four methods described above. These photographs are reproduced respectively in plates I–VII. In each case, the picture marked (a) exhibits the variations of the ultra-violet transparency, that marked (b) exhibits the blue luminescence, that marked (c) the yellow luminescence and that marked (d) the birefringence pattern as observed with a chosen orientation of the diamond between the crossed polaroids.

The composite nature of a diamond is also revealed by the spectrographic record of its infra-red transmission. Figures 1 and 2 below reproduce these records respectively for the two plates of diamond of which the photographed patterns appear in plate I and in plate II. From plate I (a) and (b), it is evident that the greater part of the oval area of this diamond is of the non-luminescent kind

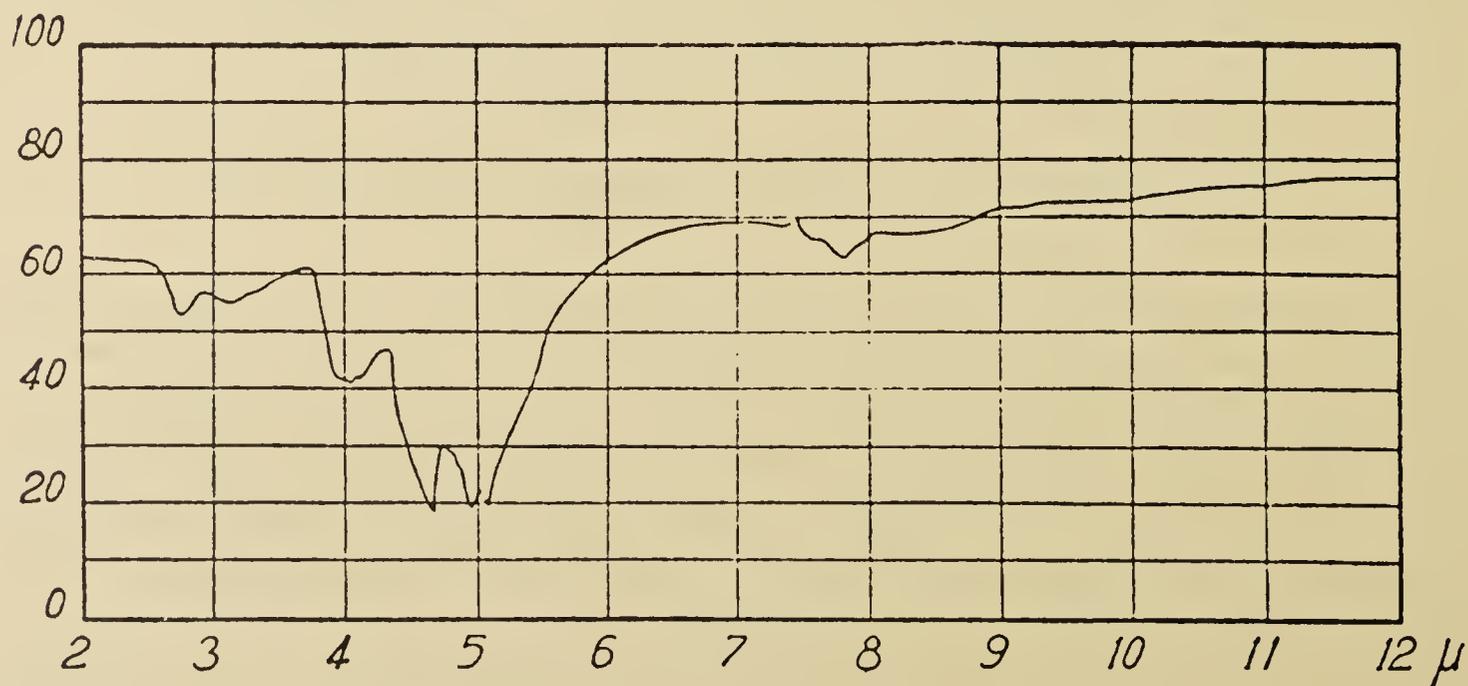


Figure 1. Infra-red absorption by composite diamond (thickness 0.83 mm).

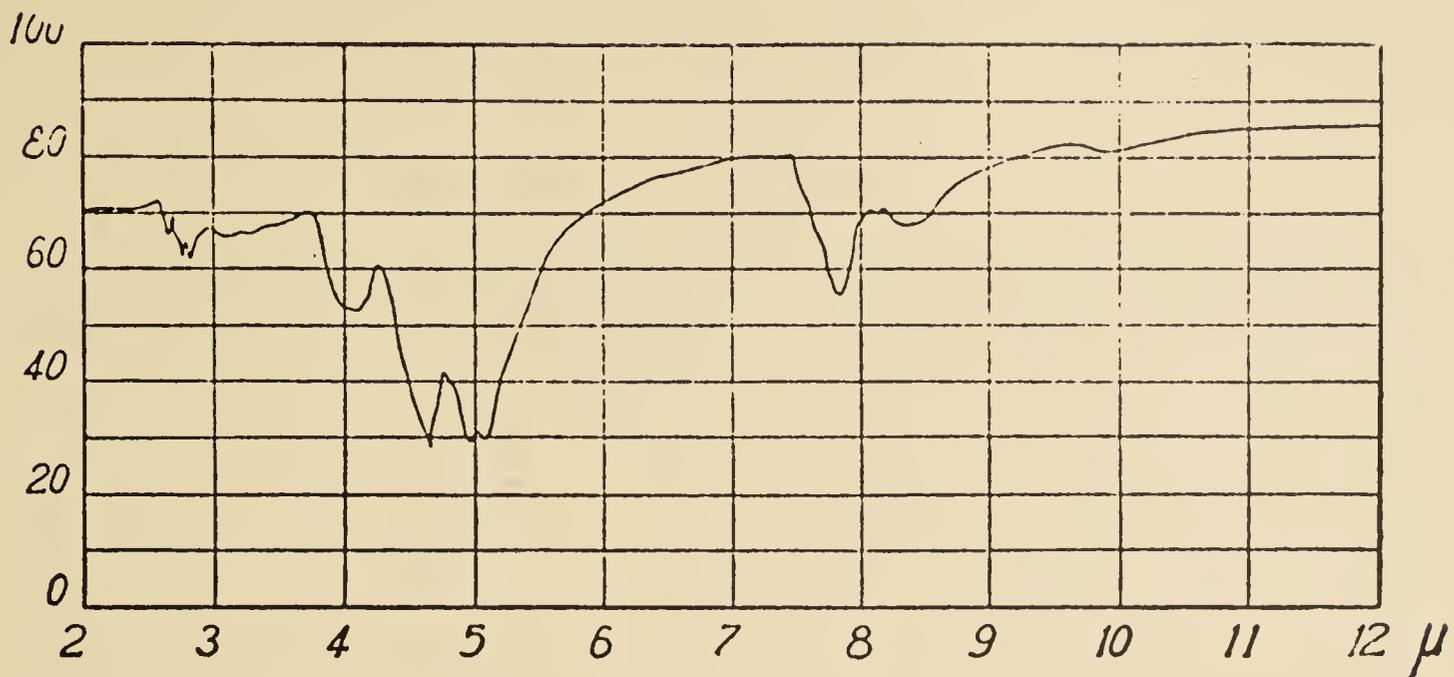


Figure 2. Infra-red absorption by composite diamond (thickness 0.81 mm).

transparent in the ultra-violet. Two sharply-defined areas, one large and another small, having the form of equilateral triangles are however seen in these figures which exhibit an opacity in the ultra-violet as well as a bright blue luminescence. The preponderance of non-luminescent diamond in this specimen is very clearly exhibited by the spectrographic record reproduced as figure 1. This shows the first-order absorption between $7\ \mu$ and $10\ \mu$ only very weakly as compared with the absorption of the second order.

On the other hand, it is evident from plate II (*a*) and (*b*) that a large part of the area of the diamond figured in it is ultra-violet opaque and blue-luminescent, while the rest is ultra-violet transparent and non-luminescent. It is, therefore, not surprising that in figure 2 which is its spectrographic chart, the first-order infra-red absorption between $7\ \mu$ and $10\ \mu$ is more strongly manifested than in figure 1.

3. The geometric character of the patterns

Examining in detail the ultra-violet transparency and blue-luminescence patterns of the several diamonds reproduced in plates I–VII, the most striking features exhibited by them are firstly the correlations between these properties manifest in the patterns, and secondly the geometric character of the patterns which is clearly related to the orientation of the octahedral or dodecahedral planes in the crystal with respect to the surfaces of the plate.

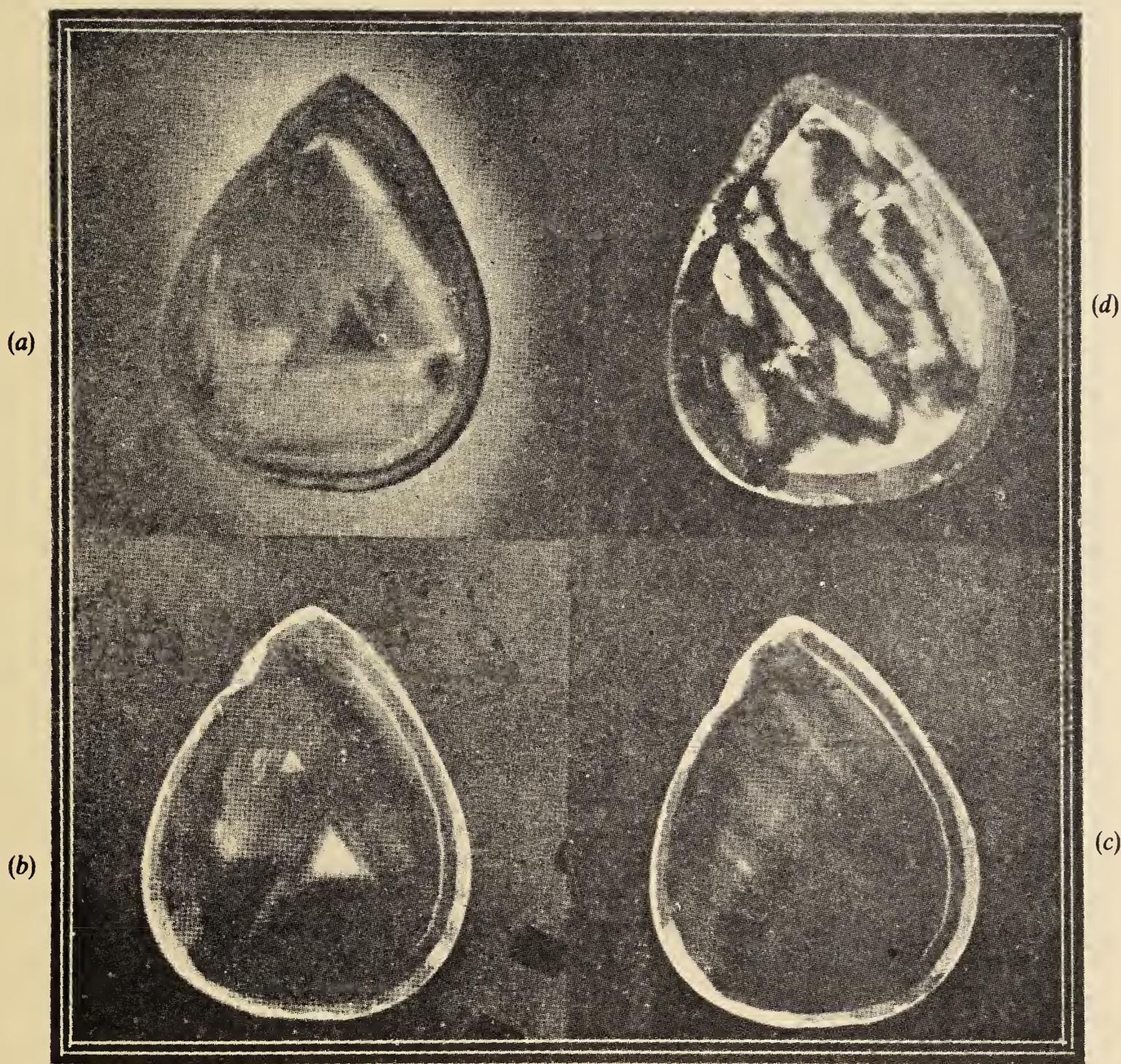
A scrutiny of the photographs reveals other features calling for mention. One of them is the kind of luminescence not exhibited by the perfect diamonds which has been described above as yellow luminescence. The pattern of yellow luminescence is usually, though not always, different from the pattern of blue luminescence. This is evident, for example, on a comparison of figures (*b*) and (*c*) in plate I, plate

III, plate V and plate VII. The yellow luminescence often takes the form of a set of parallel bands as for example in plate I, plate III, plate V and plate VII. Finally, we may draw attention to the fact that the birefringence patterns of the composite diamonds have a configuration not dissimilar to and indeed often resembling closely the other three patterns of the respective diamonds.

We shall now briefly consider what these facts of observation signify. It is well known that diamonds are usually found in nature as complete single crystals which are ordinarily not of any great size. In these circumstances, the composition and properties of any one crystal may be expected to be uniform within its interior. The actual position is rather different, as we have seen. In about ten per cent of the cases, we find diamond to exhibit a definite set of properties and in another ten per cent of the cases a different set of properties. Moreover, in a large majority of cases the crystal exhibits regions in its interior where one kind of diamond appears and other regions where the other kind appears. Further, the regions where the two kinds appear are bounded by crystallographic planes of importance, viz., the octahedral or the dodecahedral planes. The only reasonable explanation that can be put forward for this situation is that the crystal structure of diamond may assume one or another of certain alternative forms which are different but nevertheless resemble each other sufficiently to appear in juxtaposition in the same crystal. All the phenomena with which we have been confronted in our studies have to be explained on this basis.

4. Summary

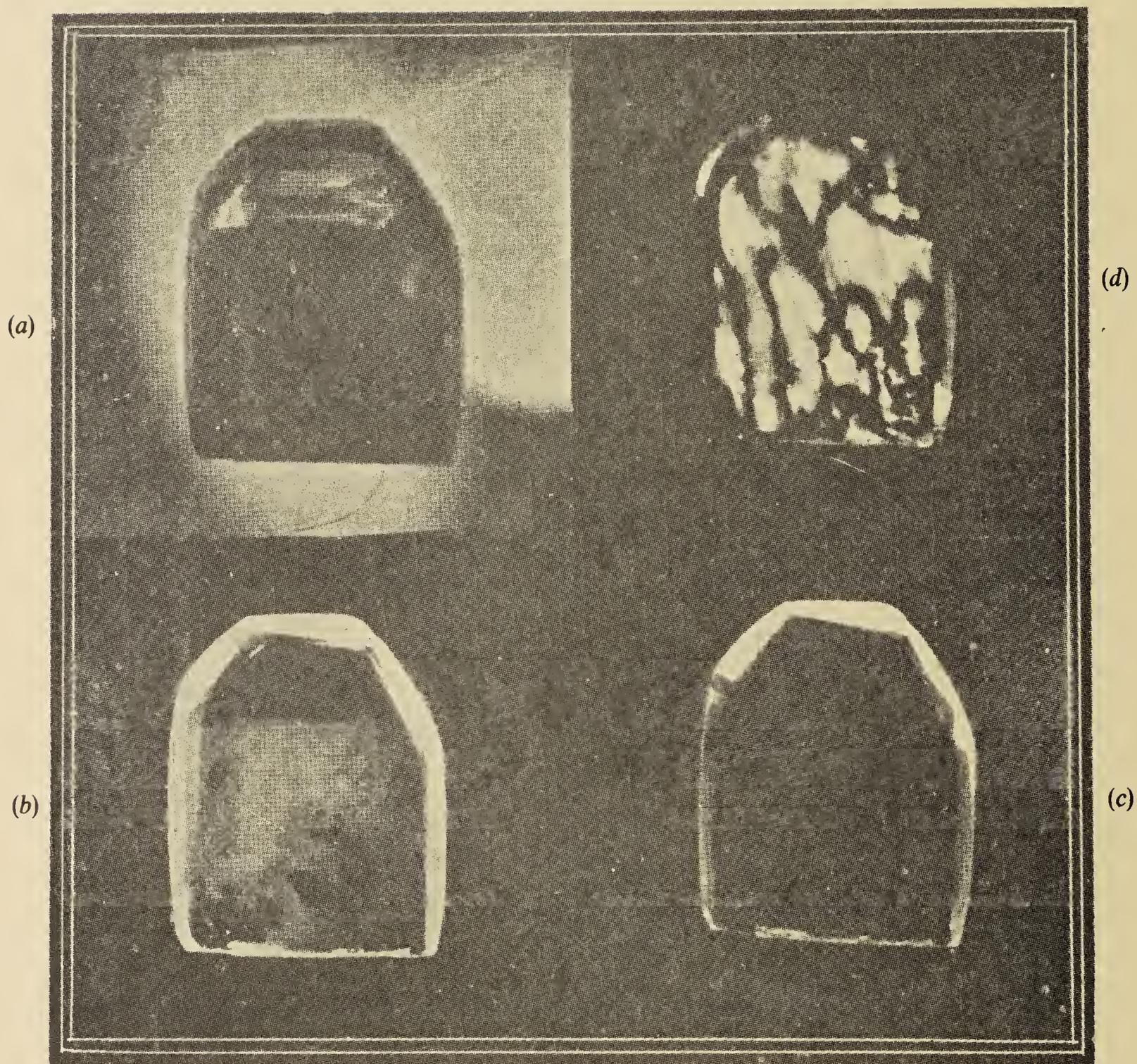
Photographs are reproduced of seven plates of composite diamond exhibiting in each case the variations over its area of the ultra-violet transparency, the blue luminescence, the yellow luminescence and the birefringence. The composite nature of the diamond is also demonstrable by the spectrographic record of its infra-red absorption. The significance of the geometric character of the patterns and of their mutual relationships is discussed.



(a) Ultra-violet transparency
(c) Yellow luminescence

(b) Blue luminescence
(d) Birefringence

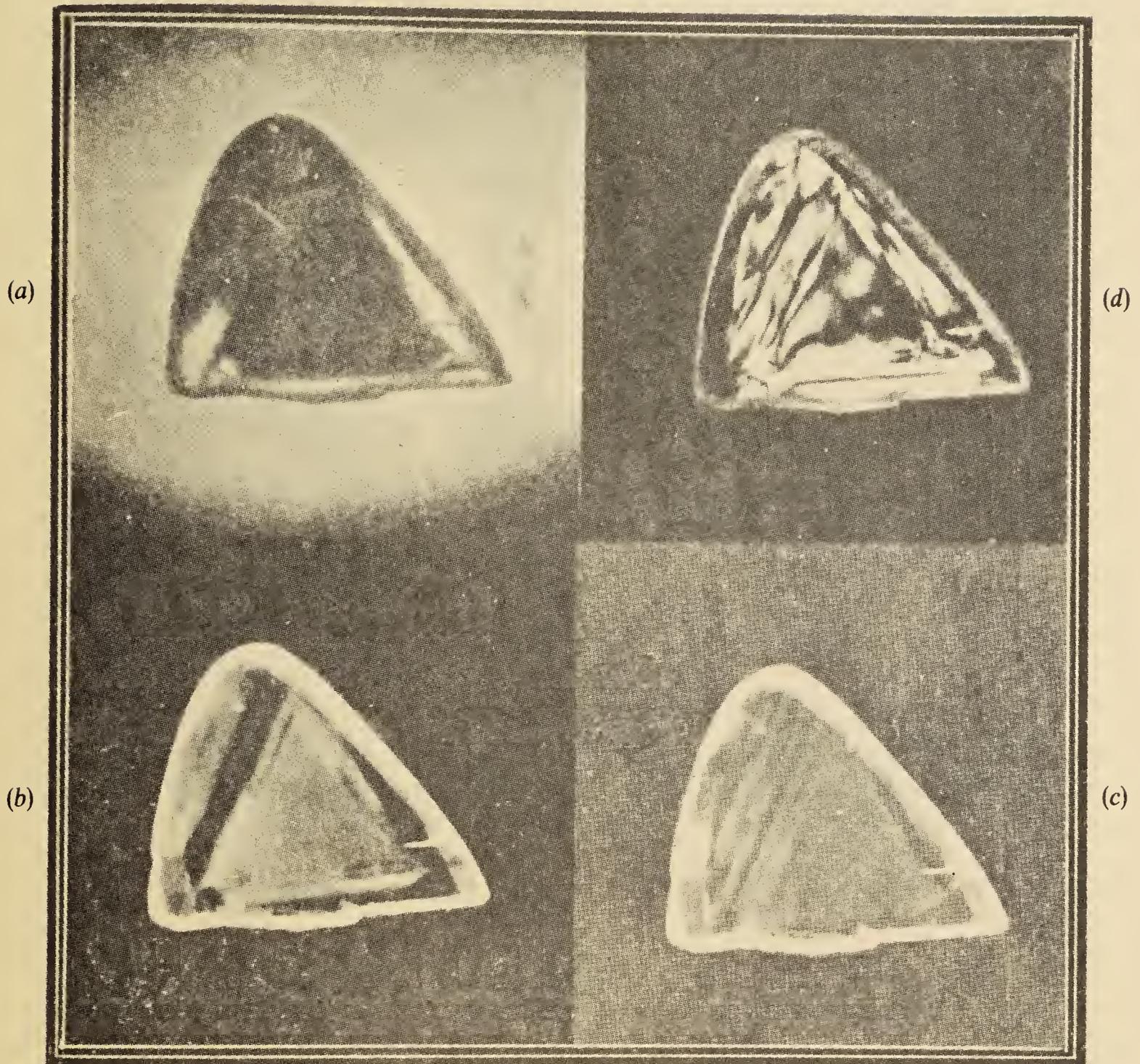
Plate I



(a) Ultra-violet transparency
(c) Yellow luminescence

(b) Blue luminescence
(d) Birefringence

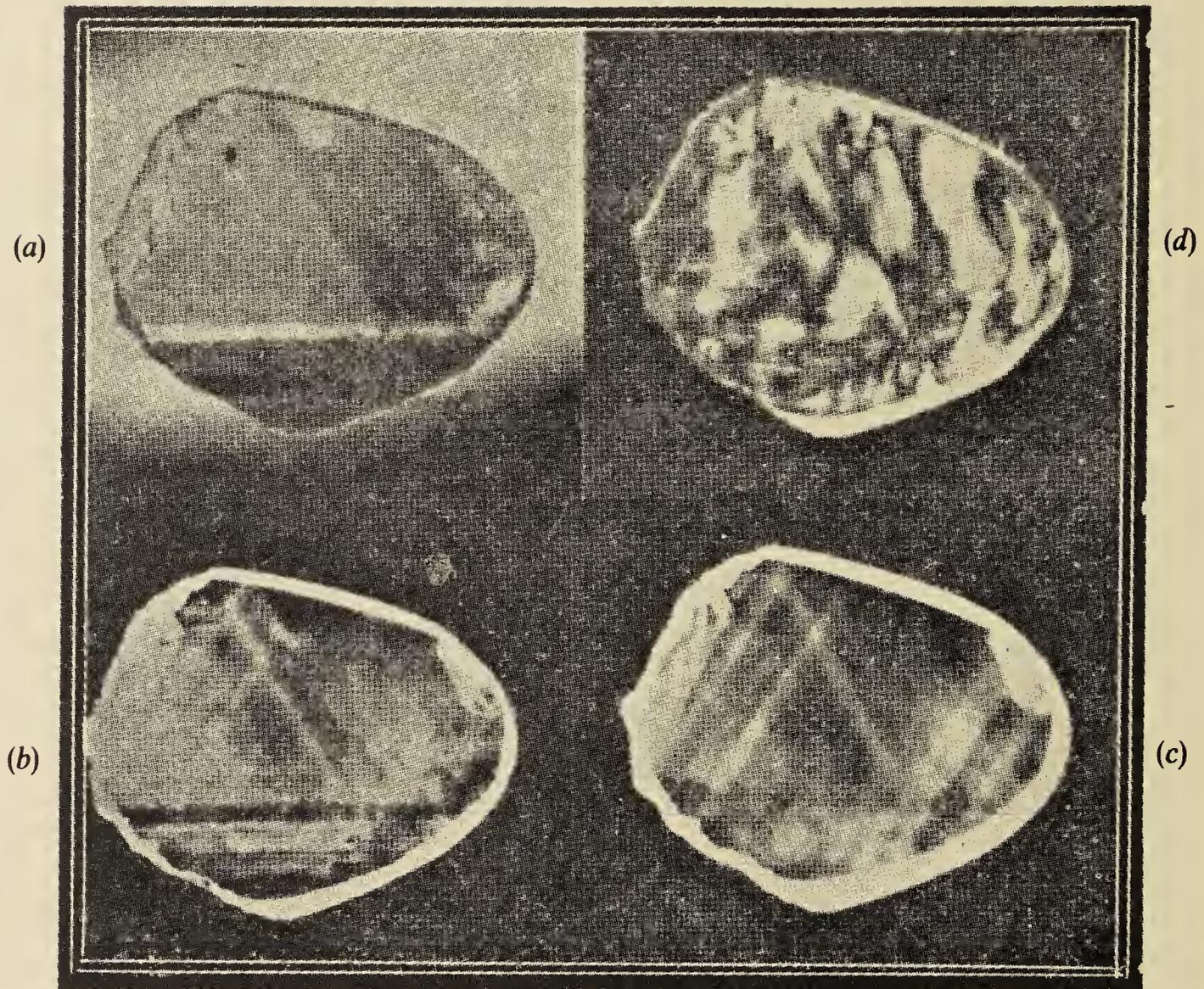
Plate II



(a) Ultra-violet transparency
(c) Yellow luminescence

(b) Blue luminescence
(d) Birefringence

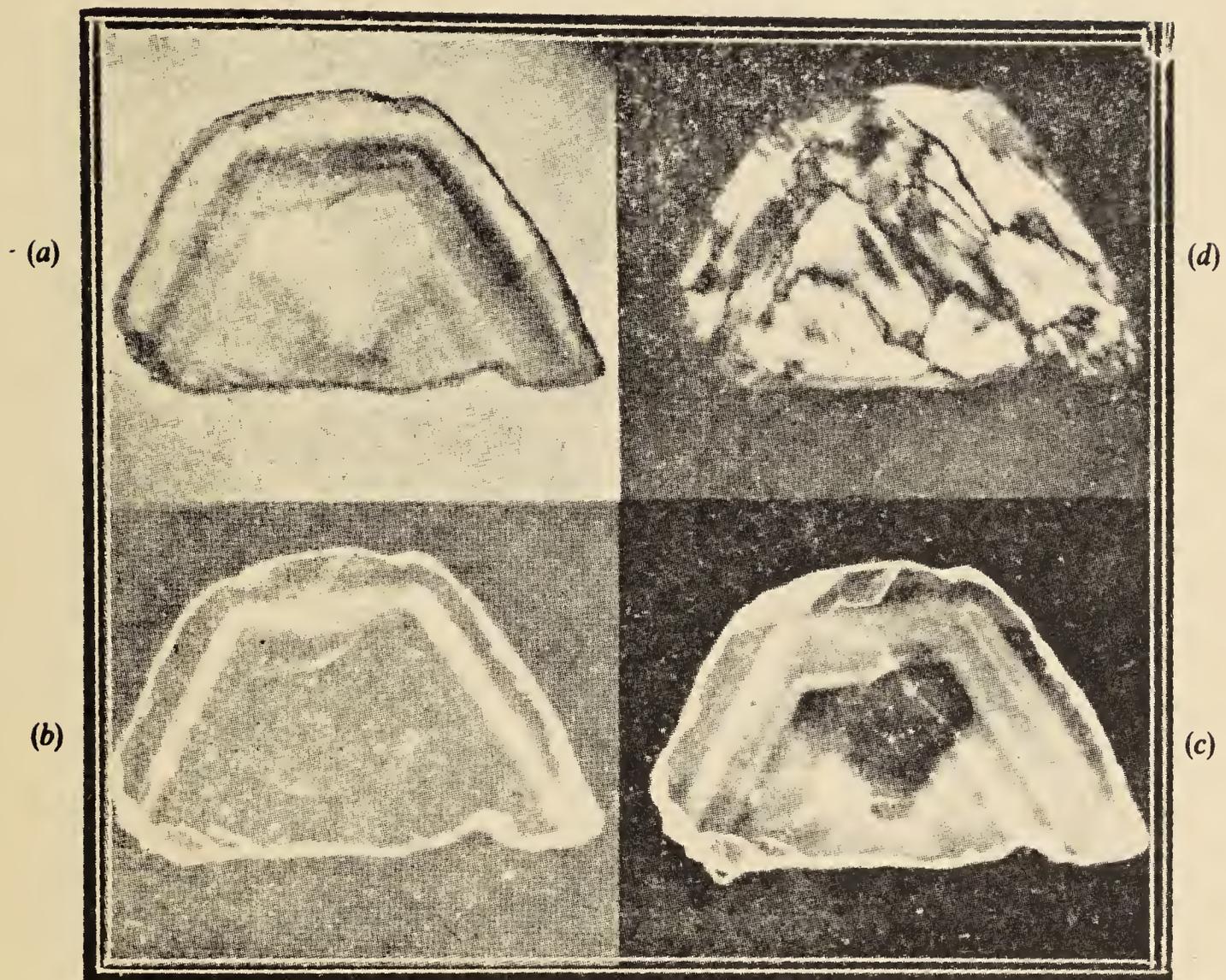
Plate III



(a) Ultra-violet transparency
(c) Yellow luminescence

(b) Blue luminescence
(d) Birefringence

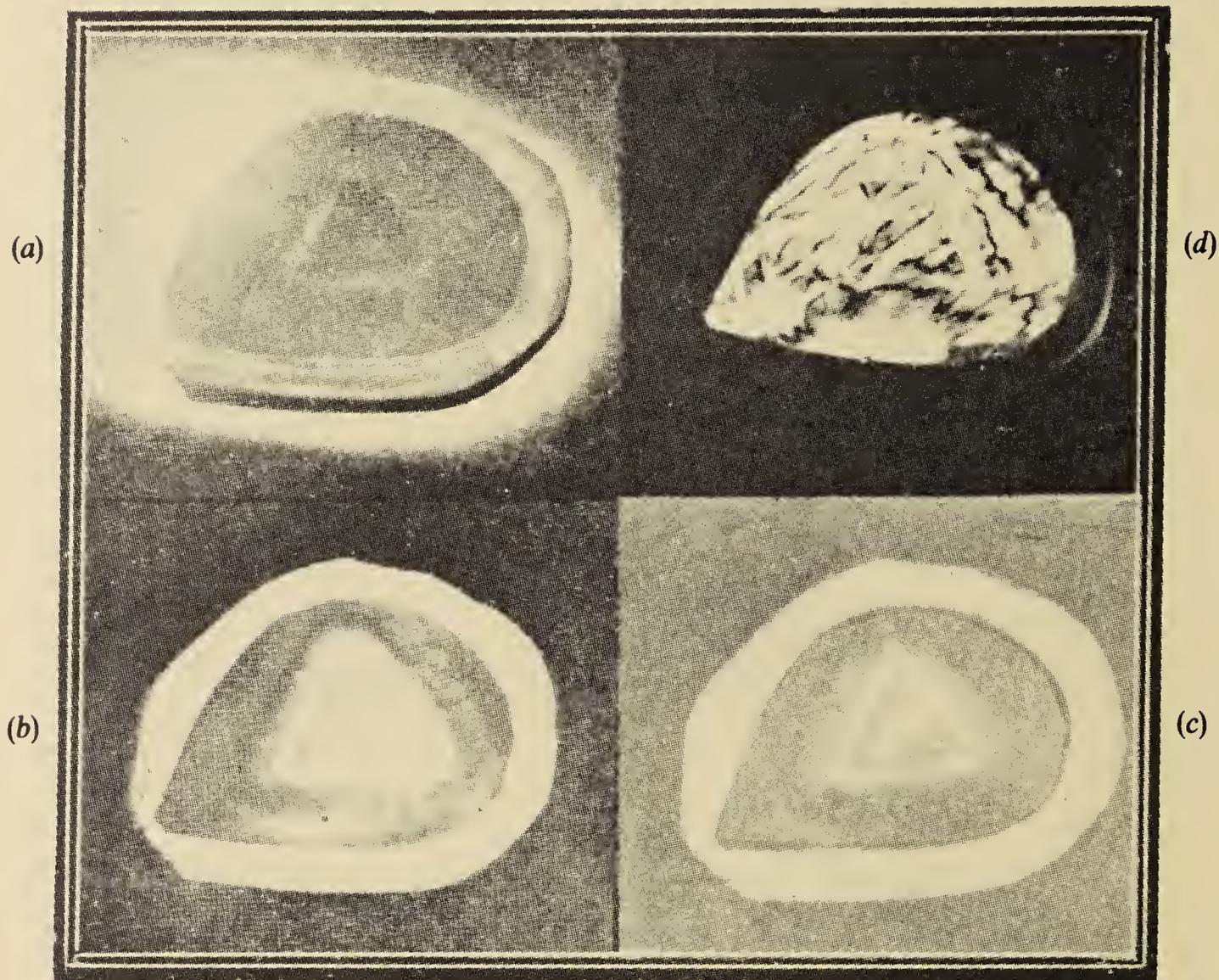
Plate IV



(a) Ultra-violet transparency
(c) Yellow luminescence

(b) Blue luminescence
(d) Birefringence

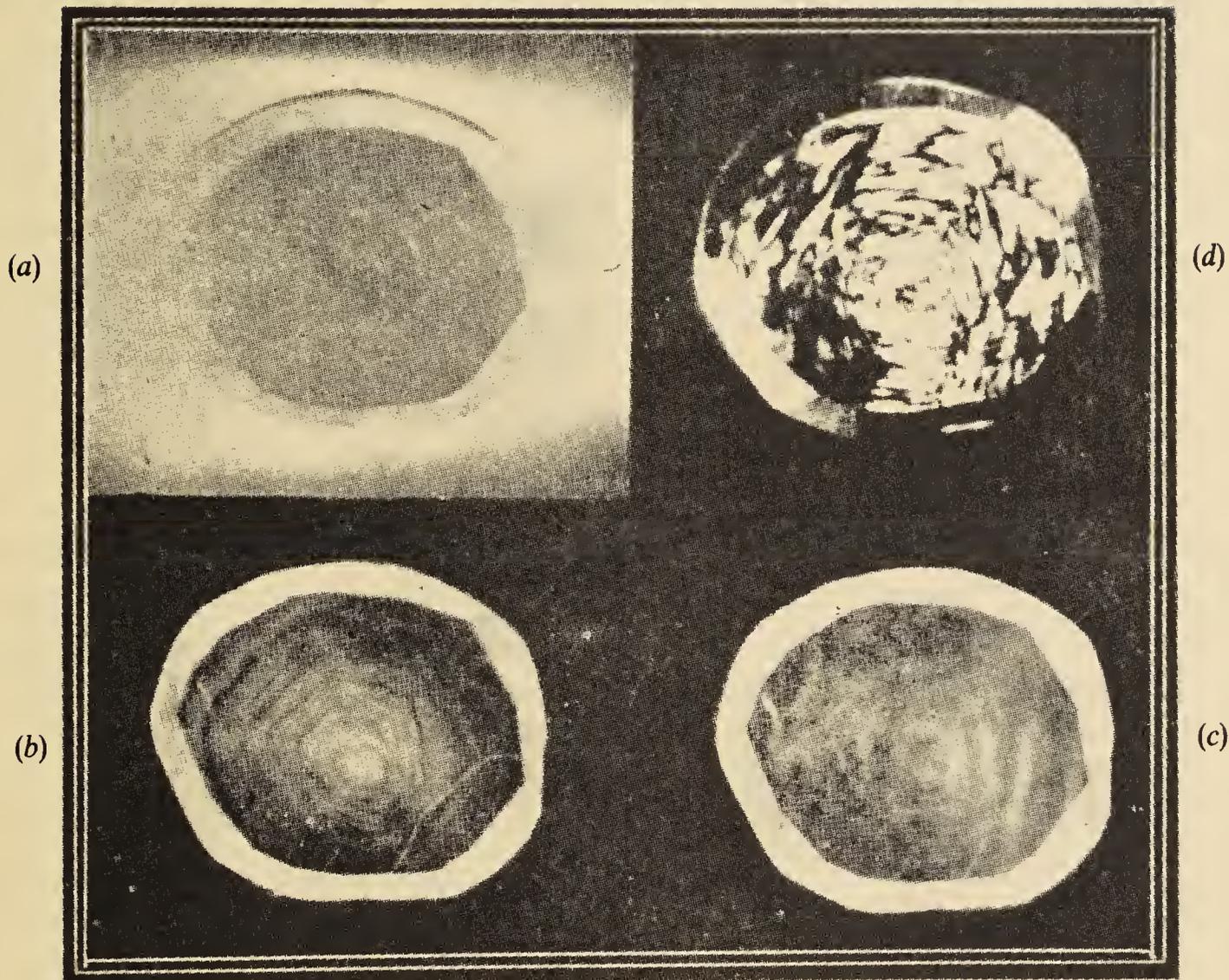
Plate V



(a) Ultra-violet transparency
(c) Yellow luminescence

(b) Blue luminescence
(d) Birefringence

Plate VI



(a) Ultra-violet transparency
(c) Yellow luminescence

(b) Blue luminescence
(d) Birefringence

Plate VII

The infra-red absorption by diamond and its significance—Part VI. The free vibrations of the structure

SIR C V RAMAN

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1. Introduction

Before we can usefully take up the discussion of the infra-red activity exhibited by diamond, we have, in the first place, to consider the dynamical behaviour of the structure of the crystal and determine the characteristic modes and frequencies of free vibration of the atomic nuclei which constitute that structure about their positions of equilibrium. The simplicity of the structure and the fact that the atomic nuclei in the crystal all have the same mass makes it possible to deal with this problem and find its solution by an elegant procedure. The basis of the treatment is the theorem in classical mechanics which states that all the possible small vibrations of a connected system of particles are a superposition of a set of normal modes in each of which all the particles oscillate with the same frequency and in the same or opposite phases, the number of the normal modes being the same as the number of dynamical degrees of freedom of movement of the particles in the system. The atomic nuclei being enormously more massive than the electrons, we are justified in considering them as simple mass-particles with the movements of which we are concerned, while the electrons in the crystal are regarded as springs which hold the nuclei in position, the strength of the springs determining the possible frequencies of vibration of the nuclei.

2. The structure of diamond

Diamond exhibits in its structure the most perfect demonstration of the validity of the concept of the tetrahedral carbon atom. Each carbon nucleus is held to four other nuclei grouped around it in an exactly tetrahedral configuration, these four other nuclei again being connected to others grouped around them in the same fashion. The structure thus built up is continued in all directions throughout the volume of the crystal. How and why this tetrahedral configuration is set up and

maintained with the perfection actually observed are questions which we shall not here enter into. They will be taken up for consideration later in our discussion of the infra-red activity of the crystal. What we are here concerned with is the ordering of the atomic nuclei within the volume of the crystal.

The structure of diamond may be described compendiously as composed of two interpenetrating face-centred cubic lattices. For our present purpose, it is more usefully regarded as composed of two interpenetrating rhombohedral lattices, eight nuclei situated at the points of each of which delineate the unit rhombohedral cell. Thus, two sets of eight nuclei, in other words, 16 nuclei taken together form the unit with the dynamical behaviour of which we are concerned in our studies. The nuclei appear in the crystal in equidistant layers parallel to its cubic planes, while in the octahedral layers the nuclei appear in layers which are alternately nearer together and further apart in the ratio of one to three.

3. The normal modes of vibration

A crystal is an extended system which is a three-dimensionally periodic array in space of structural units, each of which contains a finite number, which we shall denote by p , of non-equivalent mass-particles. The interaction of the structural units with each other has, of necessity, to be considered in considering the possible modes of vibration of these structural units. By writing down the equations of motion of the p non-equivalent particles in any one structural unit and proceeding to solve them to find their normal modes of vibration, it is readily established that there are really eight species of normal modes, all of which are comprised in the following statement: *in any one normal mode, equivalent atoms in the successive cells of the structure situated along its axes have the same amplitude of vibration and a phase which is either the same or else alternates in successive cells of the structure along one, two or all three axes of the lattice.* The alternatives for the three axes of the lattice being independent, we have $2 \times 2 \times 2$ or 8 distinct possibilities, in other words, 8 distinct species of normal modes. The same result may also be very simply derived from the consideration that the structure of the crystal is brought into coincidence with itself by a unit translation along any one axis, and hence a normal mode of vibration which is a property of the structure must also conform to the principle of translational symmetry. This is possible only if, following a unit translation, the amplitudes of vibration of equivalent atoms remain unaltered and the phases all remain unaltered or else are all reversed. This way of regarding the matter is instructive since it indicates that what we have referred to as the normal modes of vibration of the structural units may equally well be described as the stationary modes of vibration of the extended system of particles forming a periodic structure which constitutes the crystal.

The 8 sets of $3p$ equations each for the normal modes when solved give us $24p$

solutions, of which only $(24p - 3)$ represent actual vibrational modes, the 3 excluded solutions representing the translations of the group of $8p$ atoms which in effect is the dynamic unit of which the degrees of freedom appear as normal modes. In the case of diamond, $p = 2$; hence we have 45 normal modes of vibration. By reason, however, of the cubic symmetry of the structure, all of these modes are degenerate. A further simplification arises by reason of the fact that the two non-equivalent atoms have the same mass. It turns out that there are only eight distinct and discrete frequencies of free vibration of the structure of diamond corresponding to the modes described and listed below in table 1.

Table 1

Mode	Description	Degeneracy	Frequency (cm^{-1})
I	Oscillation of the two lattices in opposite phases	3	1332
II	Tangential oscillation of the octahedral planes in opposite phases	8	1273
III	Tangential oscillation of the cubic planes in opposite phases	6	1219
IV	Normal oscillation of the octahedral planes in opposite phases	4	1176
V & VI	Normal oscillation of the cubic planes in the same or opposite phases	3 + 3	1087
VII	Normal oscillations of the octahedral planes in the same phase	4	1010
VIII	Tangential oscillation of the cubic planes in the same phase	6	746
IX	Tangential oscillation of the octahedral planes in the same phase	8	624
	Translations	3	624 \rightarrow 0
	Total	48	

4. Description of the normal modes

The geometric characters of the free vibrations of the structure described and listed in table 1 may be deduced in the following manner. Considering a simple rhombohedral lattice, the eight possible situations regarding the phase of the movements at its lattice points give us firstly, a simple translation of the whole lattice, four movements in which the nuclei in the alternate octahedral planes move in opposite phases and three others which are movements of the cubic planes alternately in opposite phases. There are two rhombohedral lattices to be considered and their phases may be either the same or opposed to each other. The

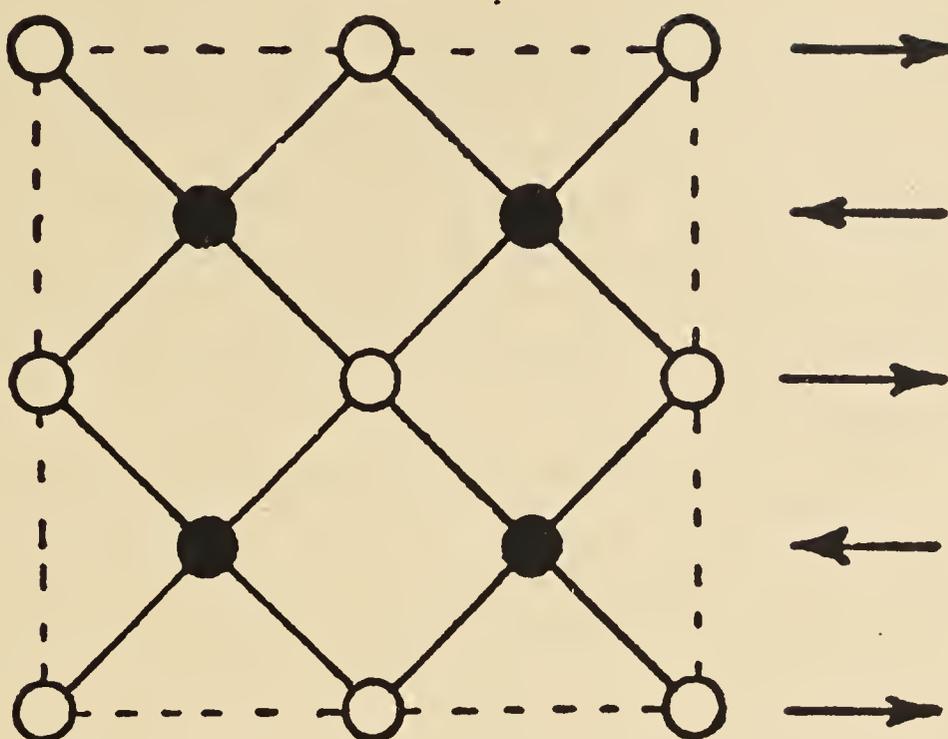


Figure 1. The triply degenerate mode of highest frequency.

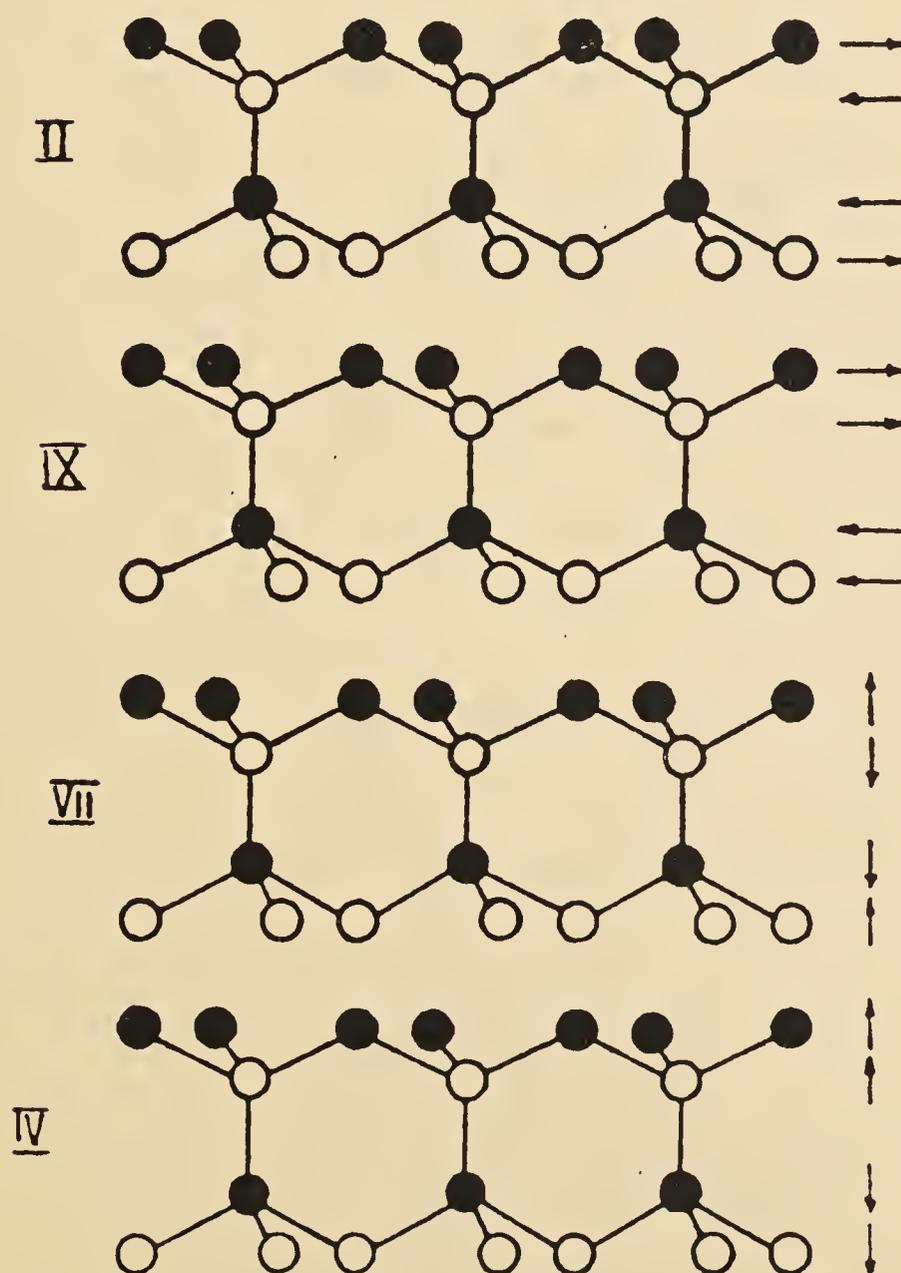


Figure 2. The four octahedral modes of oscillation.

directions in which the movements occur are determined by the symmetry of the structure. They would evidently be either normal or tangential to the layers concerned, the tangential movements being twice as numerous as the normal ones. The translations of the two lattices if in opposite phases yield a triply degenerate mode of vibration, and if in the same phase only a simple translation. Thus, in all, we have nine species of normal modes, as shown in table 1 with their respective degeneracies, but only eight distinct frequencies since the fifth and sixth modes are indistinguishable.

Figure 1 depicts the triply degenerate mode listed in table 1 as that of highest frequency. In figure 2, the four octahedral modes are depicted and in figure 3, the four cubic modes. In these diagrams, the valence bonds linking the carbon atoms with each other have been shown with a view to indicate the extent to which the movement depicted involves an extension of the valence bonds or changes in the valence-angles. We are thereby enabled to perceive at a glance whether the frequencies of the modes would be high or low and also to compare the different modes with each other.

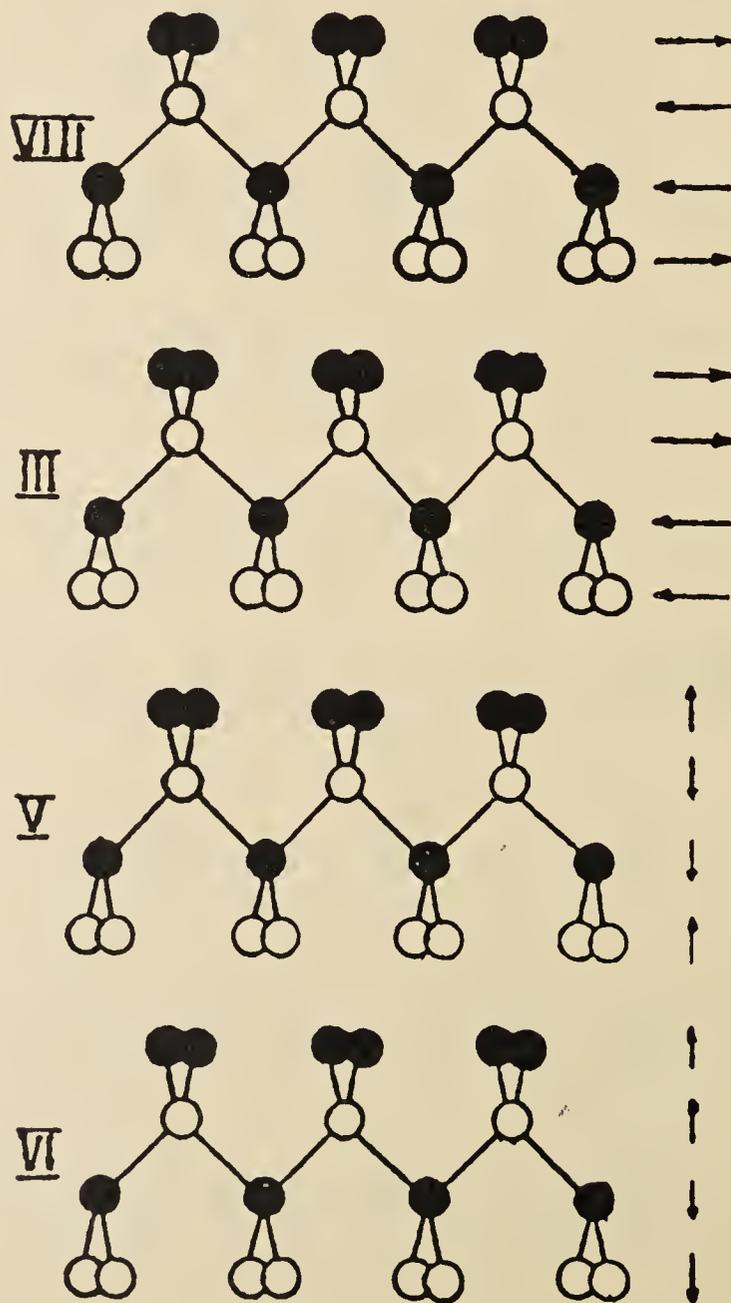


Figure 3. The four cubic modes of oscillation.

The mode depicted in figure 1 evidently involves a periodic stretching or compression of all the four bonds which connect a carbon with its four immediate neighbours, as also variations of all the bond angles. It follows that this would be the mode of highest frequency. The tangential oscillation in which the adjacent octahedral planes move in opposite phases (marked II in figure 2) involves changes in three bond-lengths and would therefore have a high frequency. It appears as mode II in the table. *Per contra* the mode in which the octahedral planes move in the same phase (marked IX in figure 2) does not involve a change in length of any of the four bonds and hence it should have the lowest frequency of all the modes. It is accordingly listed as IX in the table. The cubic mode marked as VIII in figure 3 also involves no changes in bond-lengths and would therefore be of low frequency. It appears as the last entry but one in table 1. The cubic mode marked III in figure 3 involves changes in only two bond-lengths out of the four and accordingly takes its place as the third listed in table 1. Modes IV, V, VI and VII take intermediate positions in the list which can only be determined by considerations of a quantitative character. These will be set forth in a later part of the memoir.

5. Summary

It is shown that the structure of diamond has eight discrete frequencies of free vibration. The mode of highest frequency is an oscillation of the two interpenetrating lattices of carbon nuclei with respect to each other. The other frequencies represent the oscillations of the octahedral or cubic layers in the crystal either normally or tangentially to themselves.

The infra-red absorption by diamond and its significance—Part VII. The characteristic frequencies

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1. Introduction

The four largest plates of diamond in the author's collection are roughly circular or oval in shape and have a superficial area of about 3 square centimetres each. Their thickness ranges between 1.1 and 1.5 millimetres. By recording their transmission curves in the range between $2\ \mu$ and $12\ \mu$ at the very slow speed of 10 minutes per μ of wavelength, very satisfactory records have been obtained which are reproduced in the text respectively as figures 1, 2, 3 and 4, these being arranged in the order of the increasing thickness of the plate. It should be mentioned that these plates are not perfect diamonds in the sense in which these words were used in the third part of the memoir. For, they exhibit a birefringence pattern. Tests for ultra-violet transparency however indicate that they resemble the perfect diamonds somewhat in their behaviour and this is also evident from their infra-red transmission records. We shall accordingly proceed to find from these records the eight characteristic frequencies of vibration of the structure of diamond, reserving for a later part of this memoir a discussion of the activities of these modes in respect of infra-red absorption of various orders.

As has already been explained in the previous parts of the memoir, the first-order absorption spectrum of diamond makes its appearance at $7.5\ \mu$ and extends towards greater wavelengths. Likewise, the second-order absorption commences at $3.75\ \mu$ and continues towards the region where the first-order appears. The quantitative relationships between the two orders enable us to recognise and identify the normal modes which give rise to the observed features and to determine their frequencies with considerable precision.

2. The first-order absorption

The infra-red records leave us in no doubt whatever regarding the vibrational mode of the highest frequency. In figure 3, this manifests itself as a sudden fall of

the transmission percentage from 50% at $7.4\ \mu$ to complete opacity at $7.48\ \mu$ followed by a small rise in transmission to 5% at $7.5\ \mu$, after which it diminishes again. The other figures also indicate that this absorption may be located at $7.5\ \mu$. Expressed in wave-numbers, this is $1332\ \text{cm}^{-1}$ which is also the frequency derived from studies on the scattering of light by diamond.

The position of the wavelength of the second maximum of absorption is not determinable with the same measure of precision. With thick diamond plates, the curve spreads out as it approaches the line of zero transmission. Hence, the position of this absorption peak is best determined from the records obtained with thinner plates. The mean derived from the records of several diamonds is $7.85\ \mu$ or in wave-numbers $1273\ \text{cm}^{-1}$.

Between $8\ \mu$ and $9\ \mu$, the records clearly show two other turning points, or maxima of absorption if we so choose to regard them. These may be placed at $8.2\ \mu$ and $8.5\ \mu$ respectively. In wave-numbers, these are $1219\ \text{cm}^{-1}$ and $1176\ \text{cm}^{-1}$ respectively. At greater wavelengths or lower frequencies, the transmission increases rapidly. There is an arrest in such increase between $9\ \mu$ and $9.2\ \mu$. At the latter wavelength, it becomes once again very rapid. If we take the dip at $9.1\ \mu$ to represent the characteristic wavelength, the characteristic frequency would be $1098\ \text{cm}^{-1}$. If, on the other hand, we take $9.2\ \mu$ where the curve has its greatest slope as the characteristic wavelength, the characteristic frequency would be $1087\ \text{cm}^{-1}$. At still greater wavelengths, the peak of absorption at $9.9\ \mu$ is sharply defined and the characteristic frequency can therefore be precisely stated as $1010\ \text{cm}^{-1}$.

3. The second-order absorption

There is a steep fall in transmission which is very conspicuous in the records and is particularly well shown by figure 3 and which commences at $3.75\ \mu$, or in wave-numbers $2666\ \text{cm}^{-1}$. This is just double the highest absorption frequency observed in the first order. We can therefore recognise this sudden increase in absorption of the second-order as the counterpart of the sudden increase observed in the first-order at $1332\ \text{cm}^{-1}$. This quantitative relationship demonstrates that the structure of diamond is itself responsible for the absorption spectra of both the first and the second-orders.

We have seen that in the first-order absorption the two highest characteristic frequencies of $1332\ \text{cm}^{-1}$ and $1273\ \text{cm}^{-1}$ are not fully resolved from each other, the steep rise which indicates the former joining up with the second practically over the whole of its course. Why this is so is a matter which will be considered later in this memoir. It is mentioned here for the reason if the absorptions due to these normal modes are not separated from each other in the first-order, we could scarcely expect that they would be seen clearly separated in the second-order. Following the steep increase in absorption which commences at $3.75\ \mu$ or

2666 cm^{-1} , there is an arrest at $4\ \mu$, and then a diffuse maximum at which we may locate at $4.1\ \mu$ or in wave-numbers 2439 cm^{-1} . This is exactly double the characteristic frequency of 1219 cm^{-1} which we have recognised as the third of the series in the first-order absorption, thereby confirming its determination. The diffuseness of the absorption band having its deepest point at $4.1\ \mu$ would be explained by its overlap with the second-order absorption due to the modes of vibration whose frequencies as fundamentals have been located at 1332 cm^{-1} and 1273 cm^{-1} respectively.

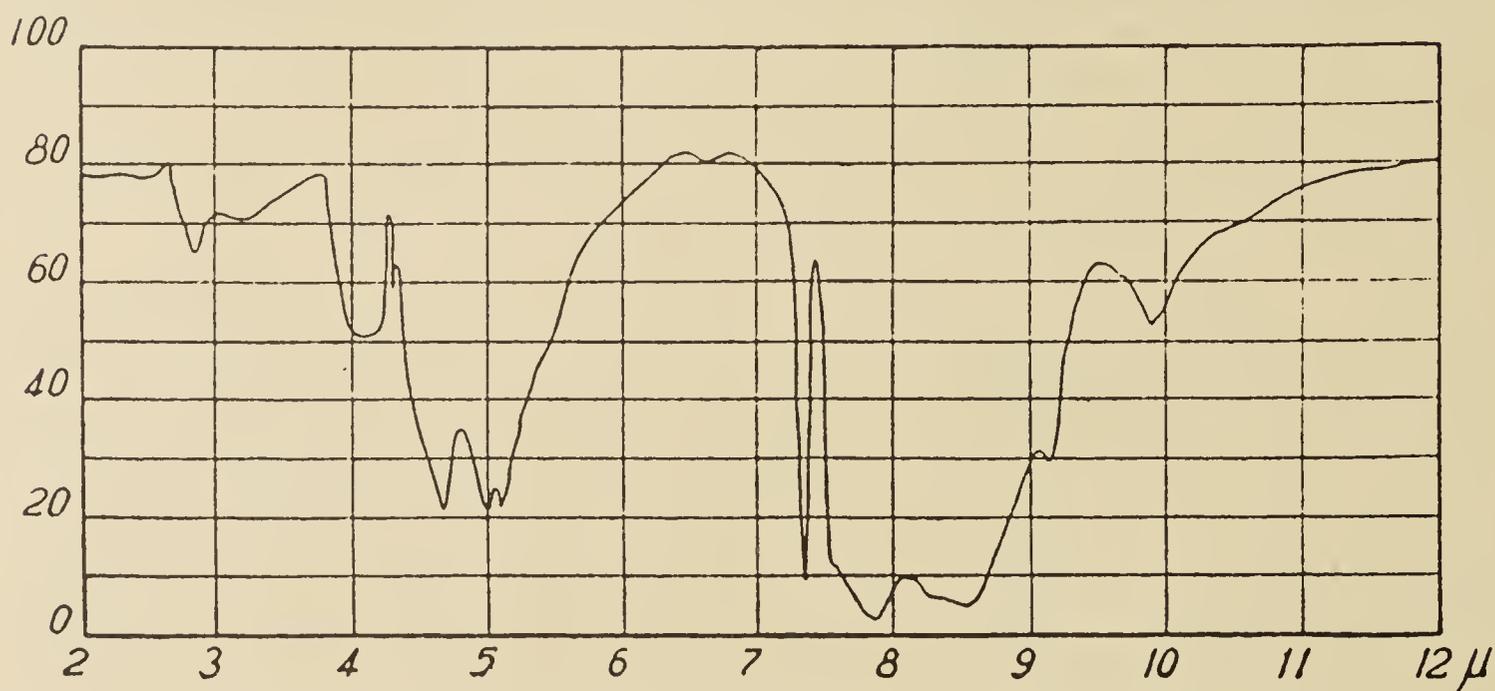


Figure 1. Percentage transmission by diamond; plate thickness 1.19 mm.

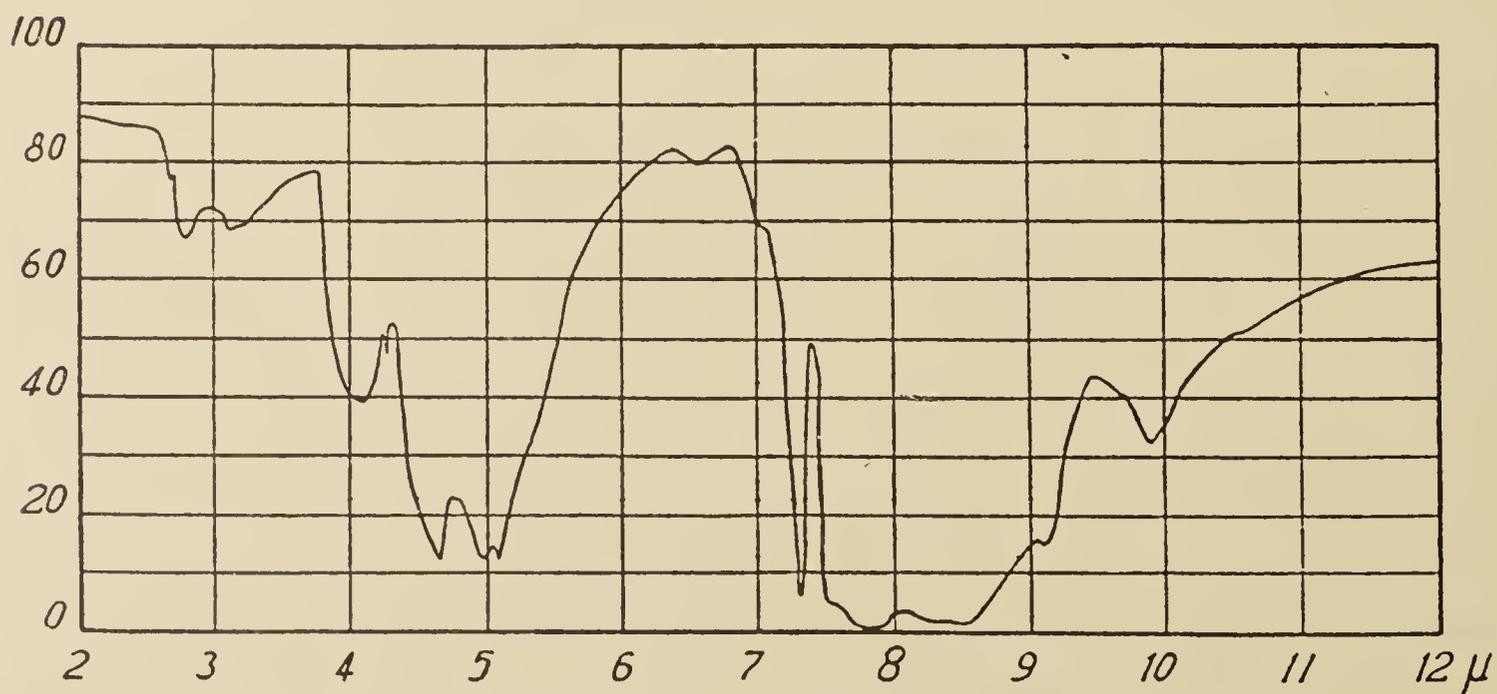


Figure 2. Percentage transmission by diamond; plate thickness 1.40 mm.

In all the four figures reproduced with this part of the memoir, a small but clear and sharply defined minimum of transmission appears between the $4.2\ \mu$ and $4.3\ \mu$

ordinates on the recording sheet. We may locate it as 4.25μ or 2352 cm^{-1} . This is very clearly the octave of the fourth characteristic mode which was located at 8.5μ or 1176 cm^{-1} in the first-order absorption, thus confirming the latter determination.

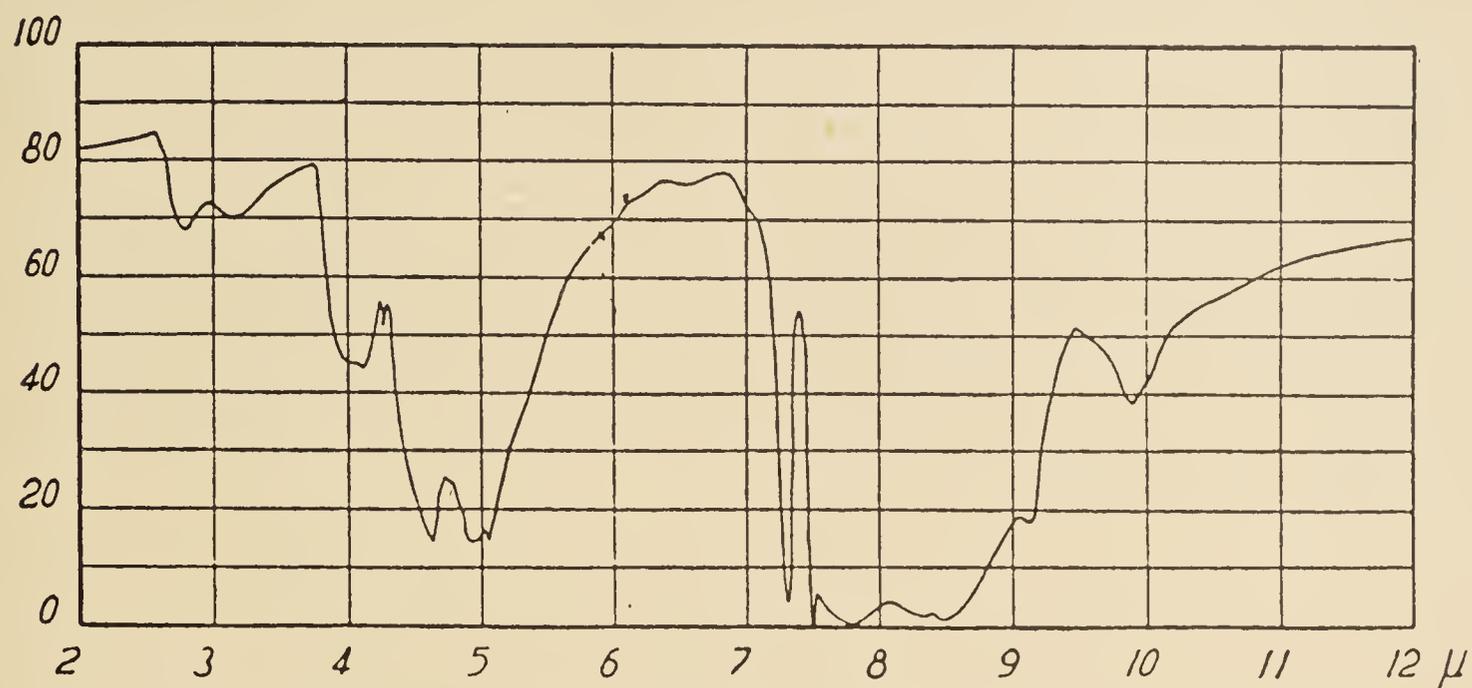


Figure 3. Percentage transmission by diamond; plate thickness 1.44 mm.

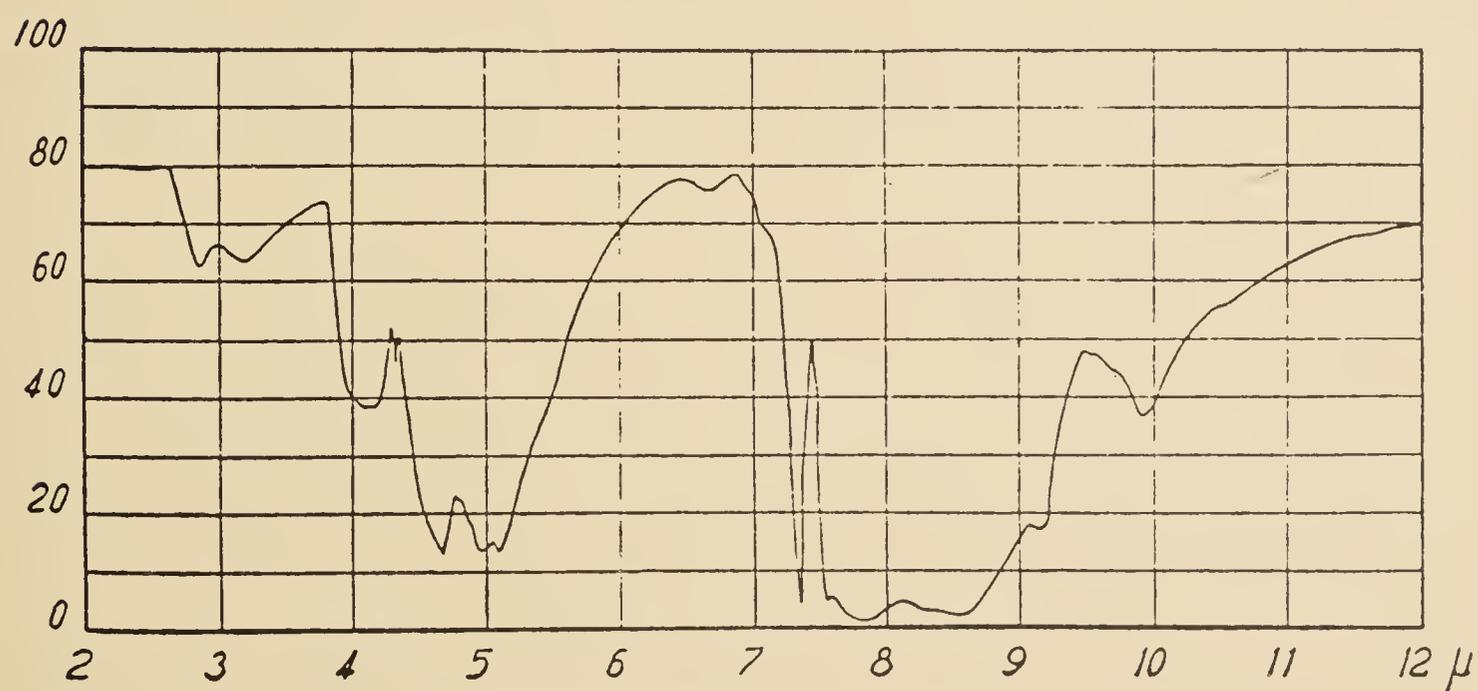


Figure 4. Percentage transmission by diamond; plate thickness 1.49 mm.

The sharply defined peak, located at 4.6μ , is the most striking feature in the records of the absorption spectra of all diamonds. Expressed in wave-numbers, this is 2173 cm^{-1} , half of which is 1087 cm^{-1} or 9.2μ when expressed as a wavelength. The wavelength at which the record of the first-order absorption has an inflexion point and exhibits its steepest fall is also 9.2μ . We are, therefore, justified in ascribing these features to the same normal mode which is responsible

for the extremely pronounced and sharp absorption peak located at 4.6μ in the second-order absorption. We accordingly recognise 1087 cm^{-1} as the fifth characteristic vibration frequency of diamond.

Another feature of the second-order absorption spectrum of diamond, quite as prominent as that considered above, is the minimum of transmission located at 4.95μ . Expressed in wave-numbers, this is 2020 cm^{-1} . This is clearly the octave of the sixth characteristic mode with its wavelength at 9.9μ or 1010 cm^{-1} already recognised in the first-order absorption. The sixth characteristic frequency of diamond of 1010 cm^{-1} is thus firmly established.

We may sum up the foregoing by the statement that the first six characteristic frequencies of diamond expressed in wave-numbers are 1332, 1273, 1219, 1176, 1087 and 1010 cm^{-1} respectively. They appear as fundamentals in the first-order absorption and with doubled frequencies in the second-order, thereby confirming the existence of the respective normal modes and enabling their frequencies to be specified with precision.

4. The seventh and eighth normal modes

In the preceding part of this memoir it was shown that the seventh and eighth normal modes would have frequencies distinctly lower than those of the other six modes by reason of the circumstance that they do not involve any changes in the length of the valence-bonds between the carbon atoms. For the same reason also, their activity in infra-red absorption should be low. Thus, it becomes a question whether any evidence would be forthcoming for the existence of these modes in the records of infra-red absorption.

The manifestation of the first six characteristic frequencies in the transmission curves is accompanied by a rapid decrease in absorption as we proceed from 7.5μ towards longer wavelengths. Indeed, the absorption at 12μ is quite small. Hence, if the seventh and eighth characteristic frequencies are lower than 850 cm^{-1} it is scarcely to be expected that their presence would be detectable in the first-order absorption spectrum. It is thus in the second-order absorption and not in the first that we should look for evidence of their presence.

Referring to the region between 6μ and 7μ in the four spectrographic records reproduced in figures 1 to 4 above, one finds in each case a small but quite definite dip in the curve of absorption of a few per cent which is located at 6.7μ , in other words at 1492 cm^{-1} . Since all the higher characteristic frequencies appear doubled in the second-order absorption, we may reasonably assume that this dip also represents the seventh characteristic mode appearing in absorption with doubled frequency. Accordingly, we recognise 746 cm^{-1} as the seventh fundamental frequency of vibration of diamond.

Recognising 746 cm^{-1} as the seventh fundamental, it becomes possible to give an acceptable explanation for other features noticed in the spectrographic

records. In the absorption spectra of all diamonds, we find that the peak at $5\ \mu$ appears doubled. The major component appearing at $4.95\ \mu$ or $2020\ \text{cm}^{-1}$ has already been recognised above as the double of the sixth characteristic frequency. The other component of the peak located at $5.09\ \mu$, in other words at $1965\ \text{cm}^{-1}$, receives a reasonable explanation as a summation of the third and seventh characteristic frequencies ($1219\ \text{cm}^{-1} + 746\ \text{cm}^{-1} = 1965\ \text{cm}^{-1}$). The appearance of this summation is clearly the result of its close approximation in frequency to the octave of the sixth fundamental which is strongly active in the second-order absorption.

Finally, we come to the explanation of the amazingly strong and sharp absorption peak at $7.3\ \mu$ noticed in all the four spectrographic records reproduced above. Recognising this absorption located at $1370\ \text{cm}^{-1}$ as a summation of the seventh and eighth fundamental frequencies, the latter comes out as $624\ \text{cm}^{-1}$. The exceptional characters of this absorption are clearly the result of its close approximation in frequency to the fundamental at $1332\ \text{cm}^{-1}$ which exhibits similarly surprising characters.

5. Summary

The absorption spectra of four exceptionally large plates of diamond which were recorded in the NaCl range of the infra-red spectrograph have been critically studied and analysed. From the study it emerges that the structure of diamond has eight characteristic frequencies of free vibration which are respectively 1332, 1273, 1219, 1176, 1087, 1010, 746 and $624\ \text{cm}^{-1}$.

The infra-red absorption by diamond and its significance—Part VIII. Dynamical theory

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1. Introduction

In the sixth part of this memoir, it was shown by dynamical reasoning of a very simple and general character that the structure of diamond possesses eight distinct monochromatic frequencies of free vibration. These modes were fully described and exhibited in figures. They were also listed in a table in the descending order of their frequencies in so far as such arrangement could be inferred from the geometry of the modes and its relation to the tetrahedral configuration of the valence-bonds of carbon.

In the foregoing or seventh part of the memoir, the actual values of the eight characteristic frequencies were determined by a study of the spectrographic records of the infra-red absorption by diamond. It is clear, however, that the association of these frequencies with the respective normal modes indicated by the dynamical theory requires further justification. It is necessary, in the first place, to show by further development of the dynamical theory that the normal modes do possess the frequencies actually exhibited in the spectrographic records. It would further be necessary to justify the individual assignments by considering the activity of the respective modes in the absorption of infra-red radiation and comparing it with the facts of observation. Reserving the latter task for the next part of the memoir, we shall proceed to consider the theoretical evaluation of the frequencies of the normal modes.

2. The first approximation

The dynamical problem with which we are concerned is very simple. We have only to write down the equations of motion of one single nucleus in the crystal, taking into account its interactions with the surrounding nuclei. The nucleus considered and the interacting nuclei have all the same amplitude and direction of movement, while the phases of movement are all either the same or opposite. The

solution of the equations of motion for the nucleus considered gives the frequency of the normal mode. The different modes differ in their frequencies by reason of the differences in the direction in which the nuclei oscillate in relation to the structure of the crystal, as also by reason of the phases of movement being different. The evaluation of the forces acting on any particular nucleus by reason of its displacements relative to the surrounding nuclei is the essence of the problem. If the resultant of these forces is known, the frequency of vibration can be written down immediately.

The interactions between two nuclei may be defined by considering the components of the relative displacement of the two nuclei and of the force of interaction between them resolved along the cubic axes of the structure and specifying the ratios of the components of force and displacement, otherwise known as the force-constants. The most important internuclear forces are evidently those arising from the displacement of the nucleus under consideration relative to the four nuclei with which it is bonded in a tetrahedral configuration by the valence forces.

The high symmetry of the structure of diamond results in all cases in a very considerable reduction in the number of force-constants appearing in the equations of motion. For instance, only two force-constants are needed to express the interactions with the four nearest neighbours. We may denote them by α and β respectively; α refers to the case in which the force and the displacement are both along the same cubic axis, while β refers to the case in which they are mutually perpendicular. The equations of motion in which α and β and the mass m of the carbon nucleus appear may be readily written down and solved. As the procedure is very simple, it will be sufficient here to set out the formulae giving the eight distinct frequencies thus obtained.

Mode I	$4\pi^2 v_1^2 c^2 m$	$= 4\alpha$
Mode II	$4\pi^2 v_2^2 c^2 m$	$= (3\alpha + \beta)$
Mode III	$4\pi^2 v_3^2 c^2 m$	$= (2\alpha + 2\beta)$
Mode IV	$4\pi^2 v_4^2 c^2 m$	$= (\alpha + 2\beta)$
Mode V and VI	$4\pi^2 v_{5,6}^2 c^2 m$	$= 2\alpha$
Mode VII	$4\pi^2 v_7^2 c^2 m$	$= (3\alpha - 2\beta)$
Mode VIII	$4\pi^2 v_8^2 c^2 m$	$= (2\alpha - 2\beta)$
Mode IX	$4\pi^2 v_9^2 c^2 m$	$= (\alpha - \beta)$

The formulae can be simplified further if the ratio α/β is regarded as known. For example, we may take α/β equal to 2, which is a reasonable assumption. All the eight frequencies can then be expressed in terms of a single constant. To find this, we may base ourselves on the frequency of mode I which is known to be 1332 cm^{-1} and then proceed to evaluate the other frequencies. We thus obtain the results shown in table 1. The calculated frequencies are all of the right order of magnitude. But they are systematically smaller than the observed values. The

Table 1. Mode and frequencies
 $\alpha = 3.14 \times 10^5$ dynes/cm $\beta = 1.57 \times 10^5$ dynes/cm

Modes	Frequency (cm^{-1}) Calculated	Frequency (cm^{-1}) Observed
I	1332	1332
II	1246	1273
III	1153	1219
IV	942	1176
V & VI	942	1087
VII	942	1010
VIII	666	746
IX	471	624

reason for this is clearly to be found in our neglect of the interactions of each nucleus with its more distant neighbours.

3. The second and third approximations

The agreement between the calculated and observed frequencies can be improved by taking into account the interactions between the particular nucleus and the twelve other nuclei which are its next nearest neighbours and are all situated at the same distance from it. All these twelve neighbours are located at the points of the same rhombohedral lattice as the nucleus under consideration. They move together with it in mode I and hence in the expression for the frequency of that mode, their interactions do not appear. The position is different with regard to the other modes listed in table 1. In every one of the latter modes, the nuclei in the alternate cubic or octahedral layers of the structure oscillate in opposite phases and hence the interactions between the nuclei located in the same lattice necessarily appear in the equations of motion. A single additional constant γ suffices to express these interactions, but it appears multiplied by different numerical factors (2 or 4 or 8) for the different modes. The formulae for the frequencies as thus corrected are given below:

Mode I	$4\pi^2 v_1^2 cm$	$= 4\alpha$
Mode II	$4\pi^2 v_2^2 cm$	$= 3\alpha + \beta + 2\gamma$
Mode III	$4\pi^2 v_3^2 cm$	$= 2\alpha + 2\beta + 4\gamma$
Mode IV	$4\pi^2 v_4^2 cm$	$= \alpha + 2\beta + 8\gamma$
Modes V and VI	$4\pi^2 v_{5,6}^2 cm$	$= 2\alpha + 8\gamma$
Mode VII	$4\pi^2 v_7^2 cm$	$= 3\alpha - 2\beta + 8\gamma$
Mode VIII	$4\pi^2 v_8^2 cm$	$= 2\alpha - 2\beta + 4\gamma$
Mode IX	$4\pi^2 v_9^2 cm$	$= \alpha - \beta - 2\gamma$

The interactions of each nucleus with the twelve other still more distant neighbours can be similarly taken care of by introducing still another constant which now appears (multiplied by a numerical factor which may be 1 or 2 or 3 or 4 as the case may be) in all the equations of motion and the formulae for the frequencies derived therefrom. These formulae are:

Mode I	$4\pi^2 v_1^2 c^2 m$	$= 4\alpha + 4\delta$
Mode II	$4\pi^2 v_2^2 c^2 m$	$= 3\alpha + \beta + 2\gamma + \delta$
Mode III	$4\pi^2 v_3^2 c^2 m$	$= 2\alpha + 2\beta + 4\gamma + 2\delta$
Mode IV	$4\pi^2 v_4^2 c^2 m$	$= \alpha + 2\beta + 8\gamma + 3\delta$
Modes V and VI	$4\pi^2 v_{5,6}^2 c^2 m$	$= 2\alpha + 8\gamma + 2\delta$
Mode VII	$4\pi^2 v_7^2 c^2 m$	$= 3\alpha - 2\beta + 8\gamma + \delta$
Mode VIII	$4\pi^2 v_8^2 c^2 m$	$= 2\alpha - 2\beta + 4\gamma + 2\delta$
Mode IX	$4\pi^2 v_9^2 c^2 m$	$= \alpha - \beta + 2\gamma + 3\delta$

4. Comparison of the calculated and observed frequencies

Whereas table 1 shows the frequencies calculated on the basis of a single constant, table 2 exhibits the results of the calculation with three constants and table 3 with four. The values of α used are the same in tables 1 and 2 and also the same as the value of $(\alpha + \delta)$ in table 3. The constants β and γ used in the three tables are also not very different. Hence, the improved agreement which is apparent between the calculated and observed frequencies is very clearly the result of taking the interactions with 4, 16 and 28 neighbours into account respectively in the three cases. It is worthy of special remark that whereas the calculated frequencies of modes IV, V, VI and VII are all the same in table 1, they show a small progressive

Table 2. Modes and frequencies
 ($\alpha = 3.14 \times 10^5$ dynes/cm; $\beta = 1.64 \times 10^5$ dynes/cm
 and $\gamma = 0.26 \times 10^5$ dynes/cm)

Modes	Frequency (cm^{-1}) Calculated	Frequency (cm^{-1}) Observed
I	1332	1332
II	1279	1273
III	1224	1219
IV	1096	1176
V & VI	1087	1087
VII	1077	1010
VIII	746	746
IX	534	624

Table 3. Modes and frequencies
 $(\alpha = 2.78 \times 10^5; \beta = 1.75 \times 10^5; \gamma = 0.25 \times 10^5;$
 $\delta = 0.36 \times 10^5 \text{ dynes/cm})$

Modes	Frequency (cm^{-1}) Calculated	Frequency (cm^{-1}) Observed
I	1332	1332
II	1244	1273
III	1233	1219
IV	1150	1176
V & VI	1081	1087
VII	1008	1010
VIII	731	746
IX	607	624

fall in table 2, but only in table 3 do they actually fall into line with the observed frequencies.

We are thus fully justified in inferring from the results of these calculations that the characteristic frequencies determined by a study of the spectroscopic records are actually the frequencies of the normal modes of vibration of the structure of diamond deduced from the dynamical theory.

5. Summary

The eight characteristic frequencies of vibration of the structure of diamond are theoretically evaluated in the first, second and third approximations, taking successively into account the interactions of each nucleus with its 4, 16 and 28 neighbours. A satisfactory agreement emerges between the calculated frequencies and those observed spectroscopically.

The infra-red absorption by diamond and its significance—Part IX. The activity of the normal modes

SIR C V RAMAN

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1. Introduction

In the preceding parts of this memoir, the infra-red behaviour of diamond in its relation to other observable properties has been fully set out, and the free vibrations of its structure have also been adequately discussed. We now proceed to consider the explanation of the one in terms of the other. Various questions here arise which need an answer. Why is there any absorption of infra-red radiation in its passage through diamond? What part do the nuclei and the electrons in its structure respectively play in this phenomenon? Why do some diamonds exhibit infra-red absorption both of the first order and of the second order, and why do others exhibit only the second-order absorption? Why do the different normal modes exhibit very different infra-red activities and why do such activities differ respectively in the first-order and second-order absorption? What is the explanation of the relationships actually observed between the infra-red behaviour of diamond and such other properties as ultra-violet transparency and luminescence? It will be our purpose in the present part of the memoir to return answers to these questions.

2. The mechanism of infra-red absorption

The absorption of infra-red radiation in its passage through a crystal involves the conversion of the energy of the electromagnetic field into vibrational energy in the solid, in other words, its degradation into heat. The spectrographic records show that the absorption is preferential with respect to certain modes or frequencies of vibration. We naturally, therefore, turn our attention first to the movements of the atomic nuclei in the crystal and consider the action of the electric field of the incident radiation on the positive charges of these massive particles. Here, however, we find in all the normal modes of vibration, that for every nucleus

which is in oscillation, there is another nucleus which is a near neighbour and oscillates with the same amplitude but in an opposite phase. Hence, considering them together, the net transference of energy from the field to the nuclei would be a vanishing quantity. In other words, the atomic nuclei do not play the primary role in infra-red absorption, and we have to recognise the electrons or negative charges in the crystal as the active agents in that process. The field of the radiation disturbs the electrons and their movements result in the nuclei being disturbed from their positions of equilibrium and set into vibration. But it is the electronic movements associated with such vibrations and not the movements of the nuclei themselves which react with the field and result in the absorption of the incident radiation.

From what has been stated, it follows that in seeking for an explanation of infra-red activity, we have to fix our attention on the movements of the electronic charge-clouds in the crystal. It is the symmetry of the distribution of the negative electric charge in its undisturbed state as well as when it is modified by the nuclear movements which determines the appearance or non-appearance of infra-red absorption and its actual magnitude when observed.

3. The second-order absorption spectrum

Since all diamonds exhibit the absorption spectrum of the second-order, it is appropriate that we first consider how such absorption arises. We may, for the present, leave out of consideration the mode of highest frequency and discuss the infra-red activity of the other modes of vibration of lower frequencies. It is a specific feature of all these modes that the alternate layers of nuclei located at the points of the same lattice oscillate in opposite phases. Hence the electrons attached to the nuclei in those layers would also oscillate in opposite phases. Hence, it might be thought that the displacements of electric charge when summed up would vanish and hence that these vibrational modes would fail to exhibit any infra-red activity. But this conclusion is subject to an important qualification, viz., the movements considered are of infinitesimally small amplitude. When this is no longer the case, the approach of any two layers towards each other and the recession of the next two layers from each other would not necessarily produce equal displacements of electric charge. Their difference would represent the resultant displacement of charge and this would evidently be periodic with *twice the frequency* of the vibrational mode. It follows that there could, in favourable circumstances, be an absorption of radiation having *double the frequency* of each of the vibrational modes under consideration. This, to put it briefly, is the explanation of the absorption spectrum of the second order exhibited by all diamonds.

Infra-red activity of the second-order demands that the normal mode under

reference should result in the negative charges suffering displacements of substantial magnitude. Whether this is actually the case would depend upon the nature of the vibration. When we compare the different normal modes with each other from this point of view, it becomes evident that their infra-red activity would be very different in the different cases. Indeed, we could without difficulty group the modes in the order of the strength of the infra-red activity which they might be expected to display.

Consider, for example, modes VIII and IX which have the two lowest frequencies, viz., 746 and 624 cm^{-1} respectively. These movements are tangential respectively to the cubic and the octahedral layers and do not involve any changes in the lengths of the valence bonds between the carbon atoms. In these circumstances, it is not to be expected that they would result in any substantial displacements of electric charge. In mode IX, the layers which move laterally with respect to each other are farthest removed, while the layers which are closer move together. Hence, this mode could exhibit no observable activity. Mode VIII is a slightly different case, since the oscillating layers are not so far apart. Hence it might exhibit a very feeble infra-red activity of the second-order.

In striking contrast with the two modes of the lowest frequency are modes V and VI which have a common frequency of 1087 cm^{-1} , and mode VII which has a frequency of 1010 cm^{-1} . Modes V and VI are oscillations of the cubic layers, while mode VII is an oscillation of the octahedral layers, in both cases in directions normal to themselves. These modes involve changes in the lengths of the valence bonds as well as changes in the bond angles and adjacent atomic layers alternately approach and recede from each other along their common normal. Hence we should expect these modes to exhibit infra-red activity of the second-order in a high degree.

Mode IV which has a frequency of 1176 cm^{-1} stands in a category by itself. It resembles mode VII in being an oscillation of the octahedral layers normal to themselves, but differs from it by reason of the fact that the layers which are close to each other move together and only the layers which are farthest apart alternately approach and recede from each other. In consequence, only one bond length out of the four changes its length periodically and all the bond angles remain unaltered. In these circumstances, we may indeed expect displacements of charge which would give rise to absorption of the second-order, but they would necessarily be very much smaller than in the case of the modes V, VI or VII.

Finally, we may consider modes II and III whose frequencies are respectively 1273 cm^{-1} and 1219 cm^{-1} . These are tangential oscillations of the octahedral and cubic layers respectively, but they involve changes of bond lengths as well as of bond angles. It follows that these modes would give rise to substantial displacements of electric charge. But their infra-red activity would necessarily be weaker than those of the modes VI and VII where the movements are normal to the layers concerned.

The foregoing remarks may be regarded as an interpretation or elucidation of

the actually observed features of the second-order spectrum of diamond described and illustrated in the seventh part of this memoir.

4. Infra-red activity of the first order

We shall now proceed to consider the activity of the principal mode of vibration having the highest frequency which is manifested by the perfect diamonds. Expressed in wave-numbers, this frequency is shown by studies on the scattering of light to be 1332 cm^{-1} . This is also the value exhibited in the first-order absorption spectrum. The feature which distinguishes this mode from the several others of lower frequencies is that the vibrations appear in the same phase in the successive cells of the structure along its axes and not alternately in opposite phases as in these other modes. As a consequence, the effects arising from the individual cells of the structure are coherent and cumulative and the observable result attains large values. We may illustrate this remark by reference to the case of magnesium oxide which has been thoroughly investigated and reported on by the author in a recent publication. MgO has a cubic structure resulting from the interpenetration of two rhombohedral lattices occupied by Mg and O respectively. The highest fundamental frequency of vibration of the MgO structure is 490 cm^{-1} . The absorbing power at the corresponding wavelength of $20.4\ \mu$ is so extremely large that radiations of that wavelength incident on the crystal are totally reflected. To exhibit the absorption spectrum of MgO in the wavelength region between $15\ \mu$ and $24\ \mu$, it is found necessary to use specially prepared films in which the absorption path does not exceed $3\ \mu$. On the other hand, the second-order absorption spectrum of MgO appearing in the wavelength region between $10\ \mu$ and $15\ \mu$ is readily recorded with plates whose thickness may be as great as one millimetre. It is evident from this that the first-order absorption of MgO is enormously more powerful than the absorption of the second-order.

Diamond, on the other hand, does not exhibit any enhanced reflecting power in the region of wavelengths between $7.5\ \mu$ and $10\ \mu$, and the fact that we can use plate thicknesses of a millimetre or more in studying its absorption spectrum in this range of wavelengths is a clear indication that the first-order absorption is extremely weak. That it is, however, not a spurious effect due to defects of structure or extraneous impurities is made abundantly clear by the facts set forth earlier in this memoir. In particular, it should be mentioned that though the first-order is weak, it is not weaker than the second-order absorption. The constancy of the relative strength of the first and second-order absorption spectra in numerous specimens of perfect diamond, and the fact that the same vibrational modes which are manifested in the first-order appear with doubled frequencies in the second-order is a clear indication that the first-order absorption exhibited by the perfect diamonds is a fundamental property of such diamonds.

The case of MgO mentioned above serves as a useful pointer in other respects

as well. The powerful infra-red activity of the first-order which MgO exhibits is a consequence of the two interpenetrating lattices in its structure carrying atoms which are different. In the case of diamond, on the other hand, the nuclei located at the points of the two interpenetrating lattices are identical. But, as has already been remarked, what we are here concerned with are the symmetry properties of the distribution of negative electric charge in the crystal. As the two lattices are constituted of nuclei carrying the same positive charge, any suggestion that one of the lattices carries a larger share of the electronic charge-cloud than the other can be ruled out immediately. Not only is such a situation inherently improbable, but it would also have consequences which are disproved by the facts of the case. Any lack of symmetry in the density of the charge distribution as between the two lattices would result in an enormously more powerful first-order absorption than that actually observed. All that we can legitimately infer from the observed infra-red behaviour is that in the structure of the diamonds which exhibit the first-order absorption, the electronic configuration, meaning thereby the variables which specify the state of the electrons in the crystal, including especially the orientations of their spins, do not conform to the requirements of octahedral symmetry, whereas in the diamonds in which the first-order absorption is absent, these requirements are satisfied.

The foregoing may be summed up by the statement that the electronic states in perfect diamonds possess only the lower or tetrahedral symmetry of the cubic class, while in the non-luminescent class of diamond they have the higher or octahedral symmetry. The situation here recognised enables us to understand the very significant relationship which is observed between the spectroscopic behaviour of diamond in regions of the spectrum which are so far apart as the infra-red between $7\ \mu$ and $12\ \mu$ and the ultra-violet between $0.2\ \mu$ and $0.3\ \mu$. If the differences in infra-red behaviour are ascribable to differences in the electronic configuration, corresponding differences are necessarily expected in the ultra-violet absorption spectra. It also becomes intelligible why the diamonds of group A and group B exhibit contrasting behaviours in respect of luminescence. Absorption of the incident radiation is a *sine qua non* for its re-emission in a modified form which is termed luminescence. Whereas diamonds of group A do absorb radiation in the near ultra-violet, group B diamonds are transparent to such radiations. It is, therefore, not surprising that group A diamonds exhibit luminescence whereas group B diamonds do not.

It may also be remarked that the inference from the infra-red data that group A diamonds possess only tetrahedral symmetry of the electronic configuration whereas group B diamonds exhibit the full octahedral symmetry receives massive support from the well-established facts regarding the crystal morphology of diamond, as well as from the phenomena of X-ray diffraction in diamond. But it would take us too far from our present theme to enter into these matters in detail. We therefore now return to a discussion of the details of the first-order absorption spectrum.

5. Characters of the first-order spectrum

As has been amply illustrated by the spectrographic records reproduced in the earlier parts of this memoir, one of the remarkable features of the first-order absorption is the sudden change from a high degree of transparency to complete or nearly complete opacity occurring at the characteristic frequency of 1332 cm^{-1} or wavelength $7.5\ \mu$. At lower frequencies or longer wavelengths, the absorption shows a progressive diminution and ceases to be significant beyond $12\ \mu$. The curve of the percentage transmission between these wavelengths represents the effect of the movements of the electronic charge-clouds in the crystal excited by the incident radiation. The changes in its course at various points indicate the influence of the nuclear vibrations of lower frequencies. The activity of these modes in the first-order absorption rapidly decreases as the difference between their frequencies and the frequency of the active fundamental of highest frequency increases. This indicates that the electronic linkages in the crystal result in a coupling between the various possible modes of vibration of the nuclei. A striking illustration of such a coupling is furnished by the astonishing intensity and sharpness of the absorption peak at $7.3\ \mu$ or 1370 cm^{-1} , which appears separated in the records from the steep increase in absorption at $7.5\ \mu$ or 1332 cm^{-1} . The absorption at 1370 cm^{-1} is clearly the result of the summation of the two lowest frequencies ($746\text{ cm}^{-1} + 624\text{ cm}^{-1}$) of the diamond structure. That it shows up in such a remarkable fashion is a consequence of its close approximation in frequency to the major absorption at 1332 cm^{-1} . It is also an impressive demonstration that the vibrational modes which manifest themselves in the infra-red absorption of diamond have sharply defined monochromatic frequencies.

6. Summary

The features appearing in the second-order absorption of diamond are discussed and explained in terms of the periodic variations with doubled frequency of the electronic charge-density resulting from the nuclear vibrations. The origin of the first-order absorption spectrum exhibited by the perfect diamonds is also discussed. The observed facts indicate that the electronic states in these diamonds possess only tetrahedral symmetry, while in the diamonds which do not show the first-order absorption exhibit the full octahedral symmetry.

The infra-red absorption by diamond and its significance—Part X. Evaluation of the specific heat

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1. Introduction

Einstein in his classic paper of 1907 introducing the quantum theory of specific heats showed that the thermal energy content of all material bodies depends in a fundamental way on the vibration frequencies of their atomic constituents in the region of the infra-red. Crystalline solids were included within the scope of his theory and the case of diamond was specially considered by him in the paper. The very striking changes which appear in the specific heat of diamond with alterations in temperature had been discovered by H F Weber in the year 1875 and Einstein made use of Weber's data to illustrate and support his theory. Assuming that the atoms in diamond had a single characteristic frequency of vibration corresponding to an infra-red wavelength of 11μ , Einstein showed that the general trend of the specific heat changes observed by Weber could be accounted for.

In the preceding parts of this memoir, it has been shown that the structure of diamond has eight specific frequencies of free vibration lying in the wavelength range between 7.5μ and 16μ . The spectrographic record of infra-red absorption by diamond enables us to recognise these frequencies and determine them with the necessary precision. It is, therefore, appropriate that we devote the concluding part of this memoir to showing that on the basis of the spectroscopically determined frequencies, and without introducing any other data or any arbitrary constants, the entire course of the variation of the specific heat of diamond over the temperature range from the absolute zero upwards to 1000°K can be computed. A comparison will also be made of the results of the computation with the latest available data on the thermal energy content of diamond.

2. The theory of Einstein

We may usefully here sketch the theory of the specific heats of crystals as envisaged by Einstein. He begins by showing that the acceptance of Planck's

radiation formula leads to the consequence that the energy of a resonator capable of absorbing or emitting radiation with a specific frequency could only increase or diminish by quanta proportional to that frequency. A procedure which enables this principle to be used for the evaluation of the thermal energy of crystals is then outlined. The thermal energy is identified with the mechanical energy of vibration of an immense number of *individual* oscillators distributed over the volume of the crystal. The total number of these oscillators is assumed to be the same as thrice the number of atoms comprised in the crystal. It is further assumed that the oscillators can be grouped into sets, each set comprising a great number of individual oscillators characterised by a common frequency of vibration. The individual oscillators in each set occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The numbers occupying these levels are in the relative proportions determined by the respective energies and by the temperature as indicated by the principle of Boltzmann. The average energy of an oscillator in each of the sets is then evaluated. Summing up over all the oscillators in each of the sets, and then over all the sets, Einstein obtained an explicit formula for the thermal energy of the crystal as a function of the temperature.

It is evident that there is adequate justification for the various steps in the foregoing argument. A crystal is an assembly of a great number of similar and similarly situated groups of atoms, the modes and frequencies of vibration of which would necessarily all be identical. The total number of degrees of dynamical freedom of the entire system may therefore be divided up into sets, each set representing a great number of individual oscillators having a common frequency. Since these oscillators are interconnected, they can exchange energy with each other and thereby constitute a system in thermodynamic equilibrium of which the behaviour could be statistically described in terms of Boltzmann's principle. The argument implies that the atomic vibration spectrum of a crystal would exhibit a set of frequencies, their number being the same as the number of sets of oscillators which are the carriers of the thermal energy. By virtue of Boltzmann's principle, the distribution of this energy over the volume of the crystal would exhibit fluctuations both in space and in time, the magnitude of the fluctuations being the greater, the higher the frequency of the oscillators under consideration.

3. The spectrum of free vibrations

The modes of free vibration of the structure of diamond were determined and described in the sixth part of this memoir. In the subsequent parts of this memoir, the characteristic frequencies of vibration as found from the spectroscopic records were assigned to their respective modes on the basis of a theoretical evaluation of the frequencies and confirmed by a comparison of the activities

theoretically to be expected with the activities actually found. We are thus on firm ground in listing the modes, their frequencies and their respective degeneracies as shown in table 1 and making the entries in the table the basis for the evaluation of the thermal energy of diamond as a function of the temperature.

Table 1. Modes, degeneracies and frequencies

Mode	Description	Degeneracy	Frequency (cm^{-1})
I	Oscillation of the two lattices in opposite phases	3	1332
II	Oscillation of the octahedral layers tangentially in opposite phases	8	1273
III	Oscillation of the cubic layers tangentially in opposite phases	6	1219
IV	Oscillation of the octahedral layers normally in the same phase	4	1176
V & VI	Oscillation of the cubic layers normally in the same or opposite phases	3 + 3	1087
VII	Oscillation of the octahedral layers normally in opposite phases	4	1010
VIII	Oscillation of the cubic layers tangentially in the same phase	6	746
IX	Oscillation of the octahedral layers tangentially in the same phase	8	624
	Translations	3	624 \rightarrow 0
Total		48	—

The 48 degrees of freedom represented in table 1 are the degrees of freedom of movement of the 16-atom group which is the dynamic unit in the structure of diamond, viz., two groups of eight atoms each located respectively at the corners of the unit cells of two interpenetrating rhombohedral lattices. All except three of these degrees of freedom are represented by discrete modes and frequencies of vibration. The three degrees left out are the three translations of the 16-atom group. They are represented in table 1 as a continuous spectrum of frequencies stretching down to zero. We shall now proceed to justify and explain this entry in greater detail.

The translations of an atomic group within a crystal would necessarily tend to displace neighbouring atomic groups and hence would set up forces resisting the movement. We are therefore led to conclude that the degrees of freedom which do not appear as internal vibrations of our dynamic units would manifest themselves as internal vibrations in elementary volumes of larger dimensions. The larger such an element of volume is, the lower would be the limit of its possible

frequencies of vibration. Hence, the translations of our atomic groups would be associated with vibrational movements in the crystal whose frequencies extend from the upper limit set by the frequencies of their internal vibration down to very low values. In other words, the vibration spectrum of diamond with its discrete set of frequencies would be supplemented by a residual spectrum which is continuous and extends down to zero frequency.

We have now to determine how the modes of vibration referred to above are distributed with respect to frequency in the residual spectrum. Low frequencies arise from internal vibrations in volume elements of large size. The number of such elements included within the crystal diminishes rapidly with increase of their linear dimensions. It follows that the density of the vibrational modes in the residual spectrum would fall off quickly as their frequency diminishes.

4. The characters of the residual spectrum

The considerations set forth above may be put into a quantitative form. Consider an element of volume whose linear dimensions are m times as great as that of our 16-atom group. The number of such groups included in the crystal being denoted by N , the number of elementary volumes whose linear dimensions are m times greater would be N/m^3 . The larger m is, the lower would be the frequencies of internal vibration in the element under consideration. We denote by ν_m , the lowest of these frequencies. If m be replaced by n , the corresponding number of volume elements would be N/n^3 and the lower limit of frequency would be denoted by ν_n . Thus the part of the vibration spectrum included between ν_m and ν_n may be ascribed to $3N(1/m^3 - 1/n^3)$ oscillators. It is evident that ν_m and ν_n would depend on the linear dimensions of the oscillators, and if we assume that $\nu_m = f/m$, and $\nu_n = f/n$, where f is a quantity having the dimensions of a frequency, we find that the spectral region between ν_m and ν_n would be associated with $3N(\nu_m^3 - \nu_n^3)/f^3$ oscillators. In the limit as m approaches n , we may write $\nu_m - \nu_n = dv$ and $(\nu_m^3 - \nu_n^3) = 3v^2dv$. Thus, the $3N$ available degrees of freedom would be distributed over the spectrum as indicated by the quantity $3N \cdot 3v^2dv/f^3$. Integrating this over the entire range of the continuous spectrum, we should regain $3N$. Thus, we find f to be the upper limit of the continuous spectrum, its lower limit being zero.

The law of distribution of frequencies in the residual spectrum thus determined rests on the assumption that the frequencies of vibration of the volume elements considered are inversely proportional to their linear dimensions. This assumption is certainly valid when the oscillators are of sufficiently large dimensions. But it should be remarked that the distribution formula deduced on the basis of the assumption shows quite clearly that the great majority of the oscillators which contribute sensibly to the thermal energy are not much larger in size than our 16-atom groups. A further remark which should also be made is that we do not distinguish between the different possible modes of vibration of the volume

elements, as for example, whether the vibrations are of the compressional or of the distortional type.

We have next to determine the value which should be assumed to be the upper limit of frequency in the residual spectrum. Since the spectrum owes its origin to the translatory movements of our 16-atom groups, the highest frequency appearing in it cannot exceed the lowest of the discrete frequencies of internal vibration of those groups which is 624 cm^{-1} . We may, therefore, provisionally assume 624 cm^{-1} to be also the upper limit at which the frequency distribution derived on the basis of our assumptions abruptly terminates. It is clear that the entire procedure is a simplification adopted to enable us to evaluate the atomic heat of diamond over the entire range of temperature in terms of well known functions of which the tabulated values are available. We shall later consider the amendments needed to bring it into closer accord with the facts.

5. The experimental data

The graph depicting the variation of the atomic heat of diamond with temperature consists of three parts. The first part appears in the low temperature range between 0° and 100° K . In this range, the atomic heat is very small, being only a few units in the second decimal place. In the second range which lies between 100° and 300° K the atomic heat rises steeply, reaching a value of about 1.5 at room temperature. The third part of the range extends from 300° K to the highest temperatures for which the experimental data are available. It is to be noted that even at 1000° K , the atomic heat is only about 5, in other words distinctly smaller than the theoretical limit of 5.94.

The measurements of H F Weber already referred to (*Philos. Mag.* **49**, 161 (1875)) showed clearly that the atomic heat of diamond falls off rapidly as the temperature is lowered, and that *per contra*, it increases as the temperature is raised but not so quickly, the graph of the variation showing a point of inflexion at about 400° K . More complete and accurate data than those of Weber in the temperature range from 275° K to 1000° K are available from the determinations by Magnus and Hodler (*Ann. Phys. (Leipzig)*, **80**, 808 (1926)). In the lower ranges of temperature, measurements have been made by K S Pitzer (*J. Chem. Phys.* **6**, 68 (1938)), by De Sorbo (*ibid.*, **21**, 876 (1953)), and most recently by Desnoyers and Morrison (*Philos. Mag.*, **3**, 42 (1958)). In the temperature range between 100° K and 300° K the measurements by these authors are in fair agreement with each other. But in the low temperature range between 0° K and 100° K where the atomic heat is very low and the measurements are therefore more difficult, there are considerable discrepancies between them. In the comparison between theory and experiment which will be made in the present memoir, we shall make use exclusively of the data of Desnoyers and Morrison, as these cover the entire range between 0° K and 278° K at short intervals. For the higher temperatures, the data

reported by Magnus and Hodler are utilized. The experimental data of these authors are presented in a summarised form in tables 2 and 3 below.

Table 2. Interpolated experimental values of atomic heats by Desnoyers and Morrison.

Temperature	20° K	30° K	40° K	50° K	60° K	70° K	80° K	90° K	100° K
Atomic heat	0.00034	0.00117	0.00285	0.00564	0.01004	0.01676	0.02635	0.04030	0.05832
Temperature	120° K	140° K	160° K	180° K	200° K	220° K	240° K	260° K	
Atomic heat	0.1115	0.1893	0.2915	0.4172	0.5624	0.7271	0.9050	1.0957	

Table 3. Experimental values of atomic heats by Magnus and Hodler.

Temperature	300° K	400° K	500° K	600° K	700° K	800° K	900° K	1000° K
Atomic heat	1.522	2.417	3.162	3.771	4.255	4.625	4.890	5.059

It is obvious that the data covering such a great range of temperature and presenting such enormous variations in the quantity measured offer a most stringent test for the theory. As has been already remarked, the evaluation of the atomic heats is based entirely on the spectroscopically determined vibration frequencies, and no use is made of any other data or arbitrary constants. It is not possible to present the comparison between the results of the theoretical computation and the experimental data with the aid of only a single graph. In the lowest part of the temperature range, such a graph would be nearly coincident with the axis along which the temperature is plotted. Even in the second part of the temperature range, the ordinates would have to be presented on a large scale for a satisfactory comparison to be possible. Accordingly, the comparison is here made in three separate figures. Figure 1 below exhibits the over-all agreement between theory and experiment, the data for the entire range of temperatures being represented on a suitable scale. In figure 2, the data for the temperature range between 0° K and 160° K are presented, a much larger scale being adopted for the ordinates. In figure 3, the temperature range between 160° K and 300° K is similarly covered, but with the ordinates drawn on a less highly enlarged scale.

6. Computation of the atomic heats

The procedure adopted for the evaluation of the atomic heat will be evident from tables 4, 5 and 6 where the calculations are shown in detail. The Einstein functions which give the atomic heat in terms of the characteristic frequencies and the absolute temperature are multiplied by their respective degeneracies and divided by 48. These are entered in the tables. The contribution of the residual

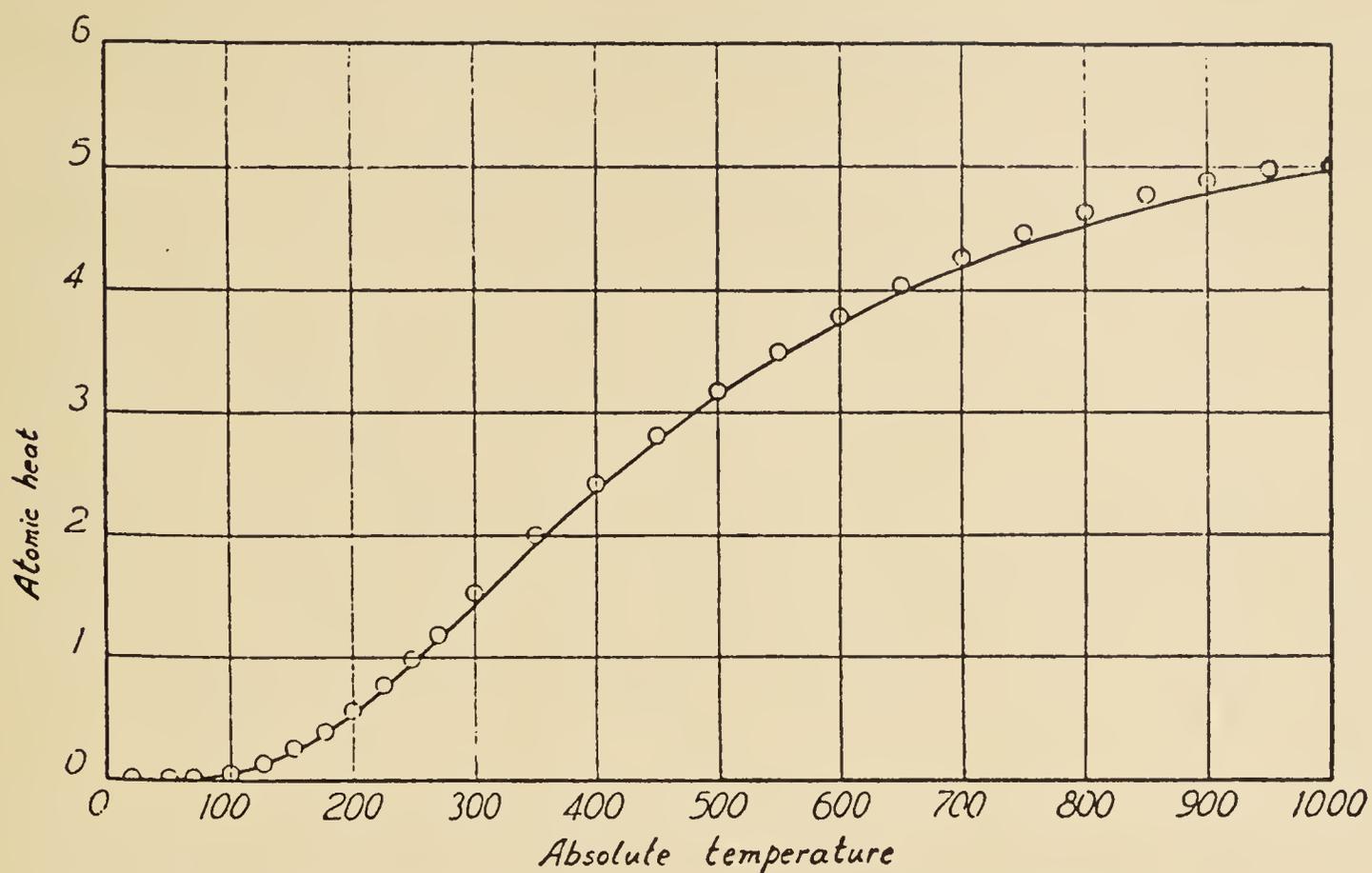


Figure 1. Comparison of calculated and observed atomic heats. Calculated atomic heats———. Experimental data ○○○○.

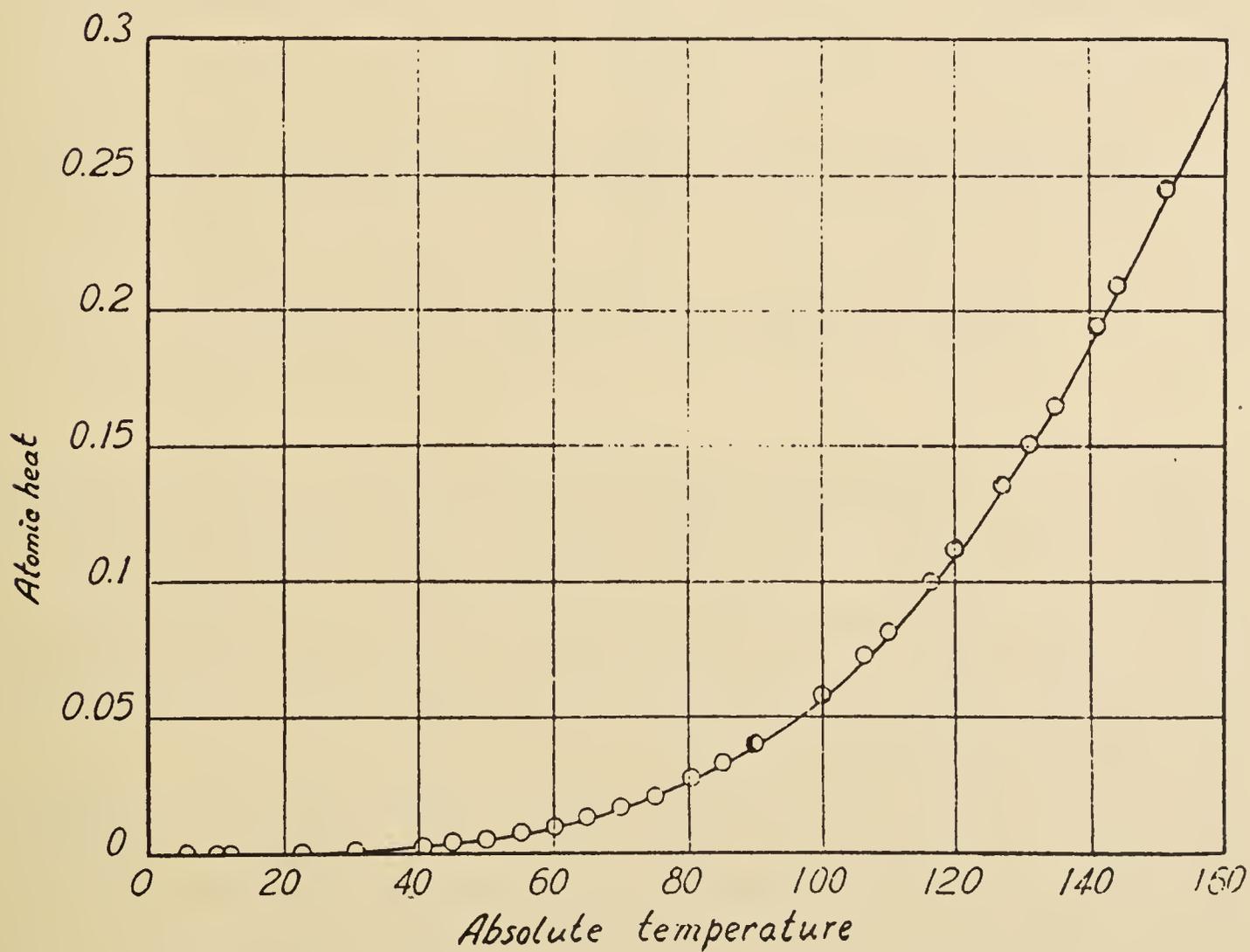


Figure 2. Comparison of calculated and observed atomic heats. Calculated atomic heats———. Experimental data ○○○○.

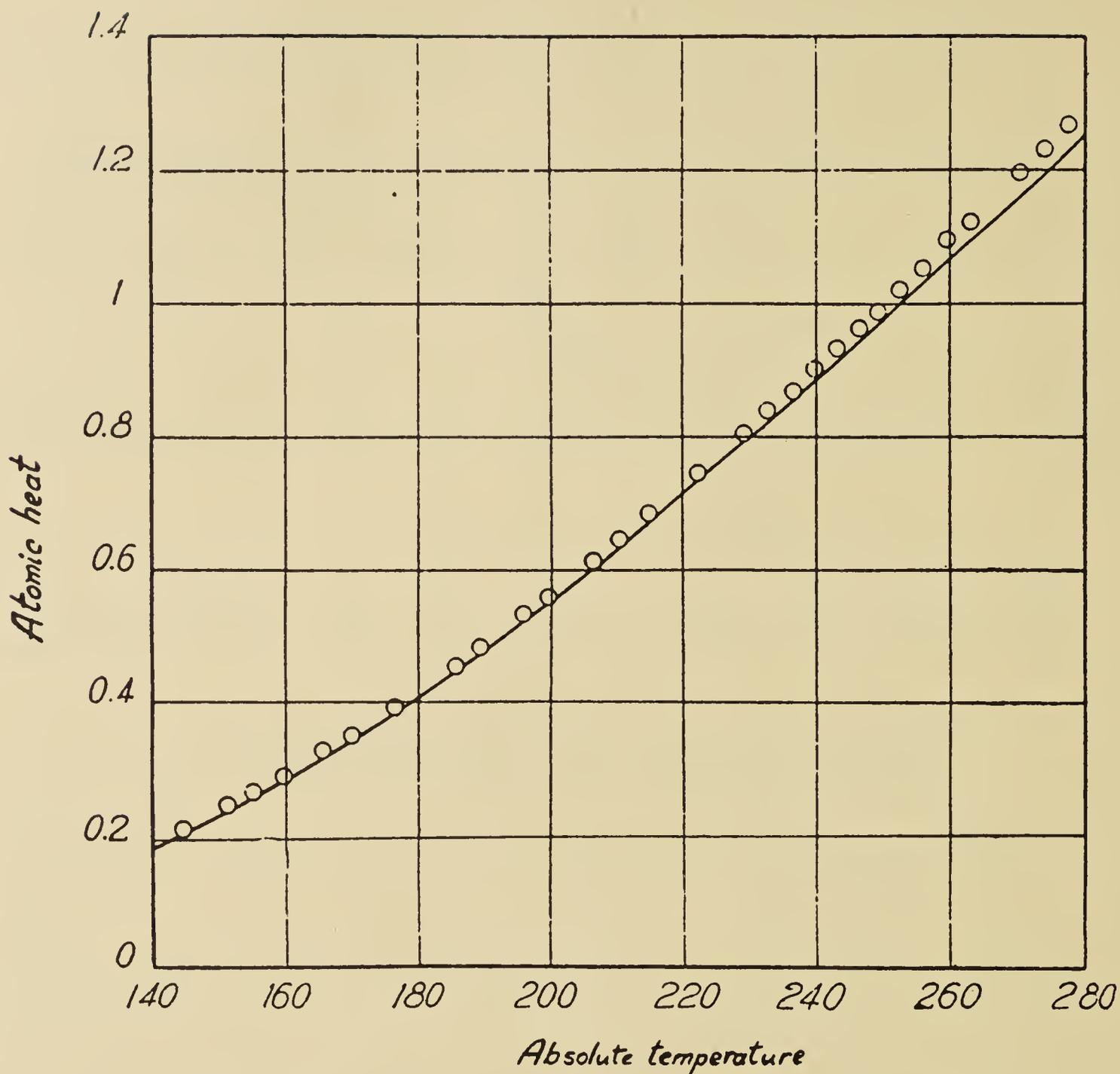


Figure 3. Comparison of calculated and observed atomic heats. Calculated atomic heats———. Experimental data ○○○○.

spectrum to the atomic heat at the respective temperatures is entered below those of the discrete frequencies. This contribution is obtained by an integration of the Einstein function multiplied by the weight-factor given by the distribution law over the whole range of frequencies appearing in the residual spectrum. The final result is divided by 48 as in the case of the discrete frequencies. It is then added to the contribution of the discrete frequencies of vibration to the atomic heat at each of the temperatures listed in the table.

It will be seen from tables 4, 5 and 6 that in the lowest part of the temperature range between 0° K and 100° K the atomic heat is determined entirely or principally by the contribution of the residual spectrum of frequencies, the discrete frequencies being altogether too high to be thermally excited. In the second part of the temperature range between 100° K and 300° K the energy of vibration associated with the discrete frequencies rapidly mounts up with rising

Table 4. Computation of the atomic heats.

	20° K	30° K	40° K	50° K	60° K	70° K	80° K	90° K	100° K
3E ₁ (1332)	—	—	—	—	—	—	—	—	—
8E ₂ (1273)	—	—	—	—	—	—	—	—	—
6E ₃ (1219)	—	—	—	—	—	—	—	—	—
4E ₄ (1176)	—	—	—	—	—	—	—	—	—
3E ₅ (1087)	—	—	—	—	—	—	—	—	—
3E ₆ (1087)	—	—	—	—	—	—	—	—	—
4E ₇ (1010)	—	—	—	—	—	—	—	—	—
6E ₈ (746)	—	—	—	—	—	—	0.0002	0.0006	0.0016
8E ₉ (624)	—	—	—	—	—	0.0004	0.0014	0.0041	0.0092
3D(624)	0.0003	0.0011	0.0025	0.0048	0.0084	0.0132	0.0195	0.0273	0.0367
Atomic heat	0.0003	0.0011	0.0025	0.0048	0.0084	0.0136	0.0211	0.0320	0.0475

Table 5. Computation of the atomic heats.

	120° K	140° K	160° K	180° K	200° K	220° K	240° K	260° K	280° K
3E ₁ (1332)	—	0.0001	0.0003	0.0009	0.0021	0.0043	0.0074	0.0118	0.0174
8E ₂ (1273)	—	0.0003	0.0012	0.0035	0.0079	0.0153	0.0259	0.0402	0.0578
6E ₃ (1219)	0.0001	0.0004	0.0014	0.0036	0.0082	0.0151	0.0248	0.0373	0.0527
4E ₄ (1176)	0.0001	0.0004	0.0013	0.0033	0.0069	0.0121	0.0200	0.0295	0.0408
3E ₅ (1087)	0.0001	0.0006	0.0018	0.0043	0.0084	0.0143	0.0220	0.0312	0.0419
3E ₆ (1087)	0.0001	0.0006	0.0018	0.0043	0.0084	0.0143	0.0220	0.0312	0.0419
4E ₇ (1010)	0.0003	0.0015	0.0042	0.0092	0.0170	0.0275	0.0405	0.0554	0.0721
6E ₈ (746)	0.0071	0.0190	0.0384	0.0646	0.0966	0.1311	0.1684	0.2042	0.2402
8E ₉ (624)	0.0289	0.0632	0.1094	0.1634	0.2219	0.2799	0.3374	0.3905	0.4401
3D(624)	0.0587	0.0838	0.1096	0.1347	0.1584	0.1796	0.1992	0.2162	0.2313
Atomic heat	0.0954	0.1699	0.2694	0.3918	0.5358	0.6935	0.8676	1.0475	1.2362

Table 6. Computation of the atomic heats.

	300° K	400° K	500° K	600° K	700° K	800° K	900° K	1000° K
3E ₁ (1332)	0.0240	0.0692	0.1201	0.1658	0.2029	0.2327	0.2560	0.2747
8E ₂ (1273)	0.0782	0.2104	0.3516	0.4713	0.5703	0.6460	0.7054	0.7501
6E ₃ (1219)	0.0700	0.1764	0.2844	0.3760	0.4465	0.5017	0.5426	0.5757
4E ₄ (1176)	0.0536	0.1371	0.2020	0.2617	0.3080	0.3436	0.3696	0.3902
3E ₅ (1087)	0.0530	0.1157	0.1712	0.2147	0.2466	0.2713	0.2895	0.3029
3E ₆ (1087)	0.0530	0.1157	0.1712	0.2147	0.2466	0.2713	0.2895	0.3029
4E ₇ (1010)	0.0896	0.1785	0.2518	0.3069	0.3482	0.3773	0.3986	0.4159
6E ₈ (746)	0.2746	0.4159	0.5086	0.5709	0.6119	0.6398	0.6589	0.6764
8E ₉ (624)	0.4862	0.6552	0.7589	0.8219	0.8643	0.8924	0.9128	0.9269
3D(624)	0.2449	0.2911	0.3173	0.3326	0.3426	0.3491	0.3540	0.3573
Atomic heat	1.4271	2.3652	3.1371	3.7365	4.1879	4.5252	4.7769	4.9730

temperature, while on the other hand, the contribution of the residual spectrum increases less rapidly; it progressively approaches its limiting value which is 1/16th of the theoretical limit for the total atomic heat.

We may here make some remarks on the comparison between the results of theory and experiment exhibited in figure 1. While there is an excellent overall agreement, divergences of a few per cent appear at temperature above 600°. The origin of these discrepancies is not far to seek. The characteristic frequencies used are those determined with the diamond held at room temperature. The changes in these frequencies which manifest themselves as the temperature is raised are small but are by no means negligible. For example, the highest frequency which is 1332 cm^{-1} at ordinary temperatures goes down to 1318 cm^{-1} at 1000°. The change is evidently associated with the thermal expansion of the crystal and it is to be expected that all the characteristic frequencies would likewise be diminished by small percentages. The atomic heats if calculated on the basis of the diminished frequencies would necessarily be greater. In view, however, of the uncertain accuracy of the experimental data at a higher temperatures, this matter will not be further pursued here.

7. The low temperature specific heats

A comparison of the figures in tables 2 and 4 shows that at the very lowest temperatures, the computed and observed atomic heats are in good agreement with each other. Disagreements however appear at higher temperatures, the calculated values being distinctly smaller than the observed ones. The percentage

Table 7. Re-computation of theoretical atomic heats.

Temperature	20° K	30° K	40° K	50° K	60° K	70° K	80° K	90° K	100° K
3D(575)	0.0004	0.0014	0.0032	0.0062	0.0106	0.0168	0.0247	0.0343	0.0456
Atomic heat	0.0004	0.0014	0.0032	0.0062	0.0106	0.0172	0.0263	0.0390	0.0564
Temperature	120° K	140° K	160° K	180° K	200° K	220° K	240° K	260° K	280° K
3D(575)	0.0713	0.0992	0.1270	0.1530	0.1769	0.1981	0.2162	0.2326	0.2467
Atomic heat	0.1081	0.1853	0.2868	0.4101	0.5543	0.7123	0.8846	1.0639	1.2516
Temperature	300° K	400° K	500° K	600° K	700° K	800° K	900° K	1000° K	
3D(575)	0.2592	0.3017	0.3246	0.3383	0.3468	0.3525	0.3566	0.3594	
Atomic heat	1.4414	2.3758	3.1444	3.7422	4.1921	4.5286	4.7795	4.9751	

differences are greatest at about 100° K and become smaller at higher temperatures. It is evident that these discrepancies arise from the assumption made in our calculations that the upper limit of frequency in the residual spectrum is the same as the lowest of the discrete frequencies of vibration, viz., 624 cm^{-1} . That a somewhat smaller value for the limit should be assumed as the basis of the calculation is indicated by various considerations, including especially the evidence furnished by studies on the blue luminescence spectra of diamond held at liquid-air temperatures. The vibration spectrum of diamond manifests itself in these spectra in combination with the electronic transition giving rise to the luminescence and it is noticed that there is a large and sudden drop in its intensity at a point distant about 575 cm^{-1} from the electronic transition. There is some justification therefore for taking 575 cm^{-1} instead of 624 cm^{-1} as the upper limit of frequency in the residual spectrum.

In figures 2 and 3, a comparison is made of the experimental data with the theoretical computed atomic heats in the lower ranges of temperature, viz., from 0° to 160° A and from 140° to 280° A, the observational values being those of Desnoyers and Morrison, and the theoretical values being those recalculated taking 575 cm^{-1} to be the upper limit of frequency in the residual spectrum, as shown in table 7. The agreement now obtained between the calculated and observed atomic heats is satisfactory. It is especially good in figure 2.

The infra-red behaviour of diamond

SIR C V RAMAN

Diamond was recognised and esteemed as a precious stone in India since ancient times. The ready cleavage parallel to the octahedral planes of the crystal which it exhibits was discovered and made use of in shaping the diamond for various purposes. Indeed, flat plates obtained by such cleavage were polished and inserted as such into jewellery with a view to exhibit the characteristic lustre of the gem. Such jewellery having gone out of fashion, it was found possible to acquire material for research in this form, which is obviously the most suitable for precise investigations on the optical properties of diamond. The four largest plates in the collection acquired by the author in the course of years are roughly circular or oval in shape and have a superficial area of about three square centimetres each. The total number of plates, a hundred in all, is sufficiently great for the collection to be considered truly representative of diamonds of the first quality.

Using polished flat plates of diamond, the following studies are readily carried out: firstly, the determination of the presence or absence of birefringence in the diamond, revealed by the restoration of light appearing when the plate is held between crossed polaroids and viewed against an extended source of light; secondly, the ultra-violet transparency or opacity of the diamond in the wavelength range between 3000 Å and 4000 Å which is readily determined by placing the diamond on a plate of fluorescent glass so as to cover it in part and observing the effect of passage of the ultra-violet rays through the diamond; thirdly, the manifestation of visible luminescence by the diamond itself under irradiation in the same range of wavelength; fourthly, the infra-red absorption spectrum of the diamond which is studied with an infra-red recording spectrophotometer in the wavelength range between 2μ and 12μ .

In a memoir¹ which has been recently published, the results of the investigation by the methods indicated above of the author's entire collection of plates of diamond have been set out, illustrated by numerous photographs and spectrophotometer records, and discussed in detail. A very clear picture emerges from the study of the close relationship which exists between all the four properties referred to and the dependence of all of them on the crystal structure of diamond. In

¹Raman, C V, "The infra-red absorption by diamond and its significance," *Memoirs of the Raman Research Institute*, No. 129. Also, *Proc. Indian Acad. Sci.*, 55, 1–61 (1962).

particular, the infra-red records made with the four largest plates in the collection and with the spectrophotometer running at its slowest speed have revealed much significant detail. In consequence, the conclusions which have emerged from the investigation have a firmly established factual basis.

Nothing in the nature of a full review of the contents of the memoir will be attempted in the present article. Its object is to present a few considerations of a general nature regarding the origin of the infra-red activity exhibited by diamond and its relation to the structure of that crystal. The perusal of the article may be useful as a preliminary to a detailed study of the memoir cited above.

The free vibrations of the structure

The structure of diamond is well known, but may be usefully recalled here. It may be described as the result of the interpenetration of two rhombohedral lattices, the points of which are occupied by atoms of carbon. The two lattices are so located with respect to each other that each carbon atom in one lattice is surrounded by four atoms in the other lattice in a tetrahedral Configuration. In the octahedral and cubic layers of the structure, the atoms belonging to the two lattices appear alternately. The octahedral layers are unequally spaced, being alternately closer together and further apart. On the other hand, the cubic layers of the structure are all equally spaced.

The absorption of infra-red radiation by a crystal is an effect arising from the interaction of the electromagnetic field in the radiation with the structural units composing the crystal. As a first step towards an understanding of this effect, it is necessary to consider the nature of the free or spontaneous vibrations of these structural units. We may deduce their modes and frequencies by the methods of classical mechanics. For this purpose, the atomic nuclei may be regarded as simple mass particles and the electronic clouds surrounding them as massless springs which hold the structure together. The relevant theory is fully set out in the memoir cited above and it is sufficient here to state the results to which it leads.

It emerges that the vibrational mode of highest frequency is one in which the two non-equivalent sets of carbon atoms oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described very simply in terms of the crystal structure. Four of the modes are oscillations of the cubic layers, while the other four modes are oscillations of the octahedral layers in the structure. The movements may be either normal or tangential to those layers and they alternate in phase as we pass from any one layer to the next equivalent layer in the structure. Since the movements of the non-equivalent atoms appearing in adjacent layers may be either in the same phase or in the opposite phases, we have eight modes in all, besides the principal mode of highest frequency already mentioned.

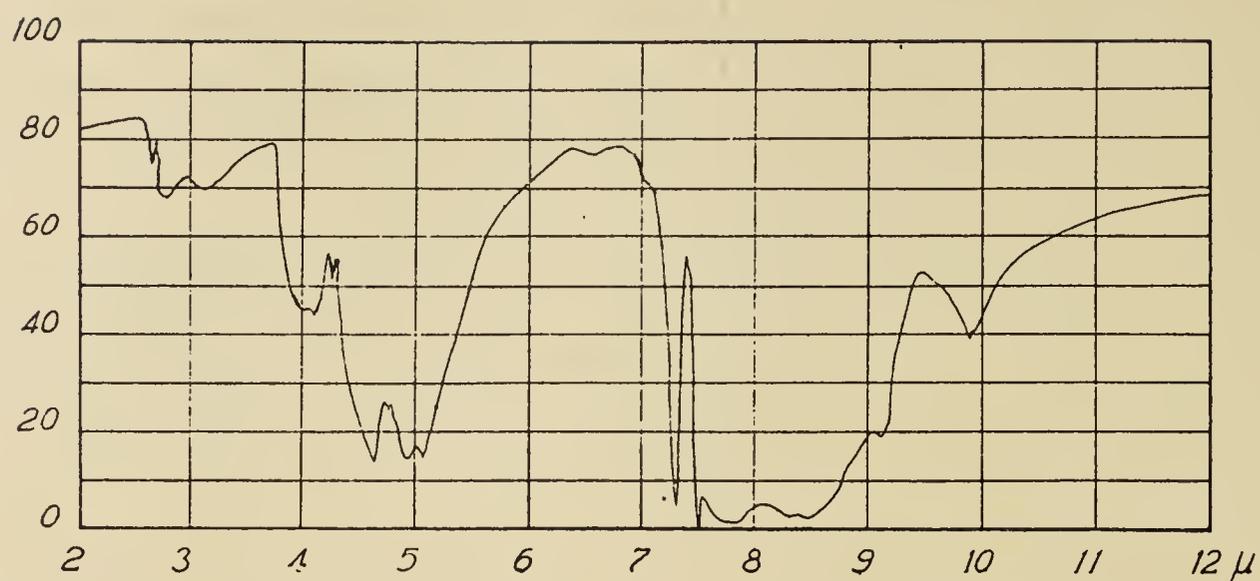


Figure 1. Infra-red absorption spectrum of diamond (plate thickness 1.44 mm).

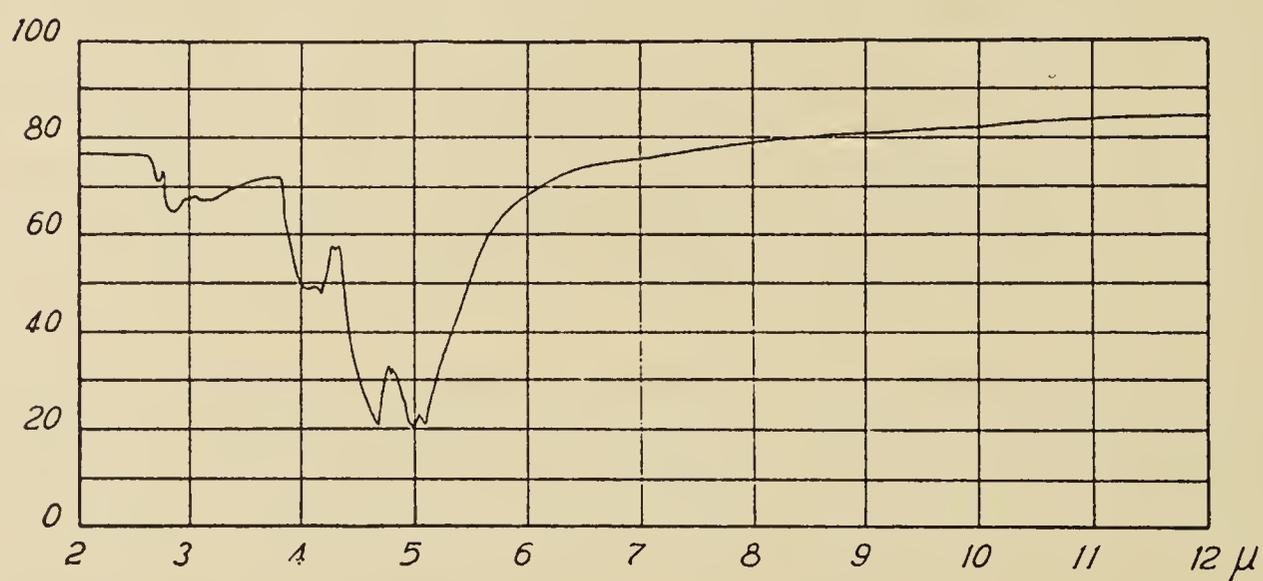


Figure 2. Infra-red absorption spectrum of diamond (plate thickness 1.06 mm).

The origin of infra-red activity

We next proceed to consider the relation between the free vibrations of the crystal and the effects arising from the passage of infra-red radiation through it. The electric field in the incident radiation acts both on the positively charged nuclei and on the negatively charged electrons. But in all the modes of vibration with which we are concerned, there are as many positively charged nuclei moving in one phase as there are others moving in the opposite phase and with an equal amplitude of vibration. It follows as a consequence that the displacements of positive charge when totalled up cancel out in all the modes under consideration. Hence, the free vibrations of the structure cannot be excited by the forces exerted

by the field on the atomic nuclei. Necessarily, therefore, the movements of the atomic nuclei can have no effect on the radiation passing through the crystal. We conclude that the infra-red activity of the crystal arises solely by reason of the forces exerted by the field on the negatively charged electrons and of the resulting movements; such activity is only possible when the displacements of negative charge produced do not cancel out when summed up over each structural unit.

Since the electrons are held in position by their interactions with each other and with the positively charged nuclei, the displacements of negative charge would necessarily disturb the nuclei from their positions of equilibrium. But the nuclear movements thus arising would not contribute to the infra-red activity. Thus, while in the free vibrations of the structure, the massive positively charged nuclei play the leading role and the electrons a subsidiary one, the situation is reversed in respect of the infra-red activity, the electrons here playing the leading role and the nuclei a subsidiary one. In other words, the spectrum of infra-red absorption are essentially different in their nature and origin. Being both properties of the same structure, we may expect to find some resemblances, but nothing in the nature of an identity or complete correspondence is to be expected.

From what has been stated, it follows that in seeking for an explanation of the infra-red activity of diamond, we have to fix our attention on the electronic charge-clouds in the crystal. It is the distribution of the negative electric charges in its undisturbed state as well as when it is modified by the nuclear movements which would determine the appearance or non-appearance of infra-red absorption and its actual magnitude when observed.

The electronic configuration

Diamond exhibits in its structure a perfect demonstration of the validity of the concept of the tetrahedral carbon atom. For, the four valence bonds joining each carbon atom with its four nearest neighbours are parallel to the four tetrahedral axes of the crystal. There is no reason to believe or assume that the two sets of carbon atoms thus linked together are in any way different from each other. Indeed, we may take it for granted that both sets of atomic nuclei have associated with them equal distributions of negative charge. But it would not necessarily follow from this that the electronic configuration in the crystal would exhibit centres of symmetry located at the midpoints between every pair of adjacent atoms in the structure. For, we have to consider not only the static distribution of negative charge but also the movements of the electrons linking the carbon atoms and circling around the four tetrahedral axes of the structure. These movements would be such that the structure as a whole is diamagnetic. The tetrahedral setting of the axes of the structure ensures that whatever be the sense of the electronic movements about these axes, the magnetic moments arising therefrom

would cancel out completely, provided the sense of the movements is the same for all four axes. This leaves the sense of the movements of the individual electrons in each pair forming a valence bond, an open question. If the senses of the movements of the two electrons are opposed to each other, then both in the static and dynamic pictures, there would be a centre of symmetry located at the midpoint between the nuclei under consideration. But, if on the other hand, the senses of the movements of the two electrons around the tetrahedral axes are the same, then there could be no centre of symmetry located at that point.

Thus, considerations of a very general nature indicate the possibility of the structure of diamond either possessing or not possessing the maximum symmetry of the cubic system. In other words, diamonds may belong either to the octahedral or to the tetrahedral class of that system. This is indeed the case as is evident from studies on the naturally occurring crystal forms of diamond, as also from studies of the various physical properties of diamond which are influenced by the symmetry of the electronic configuration within the crystal. In particular, spectroscopic theory indicates that studies of the infra-red behaviour of diamond should yield clear and unquestionable evidence bearing on this issue.

The effects of crystal symmetry

If the midpoint between every pair of adjoining carbon atoms in the crystal is a centre of symmetry, it follows that the principal mode of oscillation of the structure in which the two sets of atoms move with equal amplitudes but in opposite phases would not give rise to any displacement of electric charge. Hence, the frequency of this mode would fail to manifest itself in the absorption of infra-red radiation. The frequencies of the remaining eight modes of vibration would also fail to appear, but for a wholly different reason. In each of these eight modes, the phase of the movement is reversed as between any one layer of atoms and the next equivalent layer. The displacement of charge resulting from the relative displacement of two adjacent layers of atoms in the crystal would be cancelled out by the displacement in the opposite direction due to the next pair of equivalent layers. It should be remarked however that such cancellation would be complete only in the first approximation. If the finiteness of the amplitudes of oscillation in the structural units is taken into account, there would be a difference left over, as a consequence of which each of the eight modes would be active in the second approximation. Hence, they would manifest themselves in absorption with doubled frequencies.

The strength of the second-order effect referred to above would necessarily be different for each of the eight different modes of vibration, since it would depend on the movement of charge resulting from the approach or recession of the adjacent layers of atoms in the crystal. As has already been remarked, the spacing

of these layers is different in the cubic and octahedral planes and in the latter case alternates between two very different values. Since the movements of the layers may be either normal or tangential to the layers, very large differences may be expected between the magnitudes of the second-order infra-red activities of the eight modes. Thus, the situation may be summed up by the statement that the centro-symmetric diamonds would fail to exhibit any infra-red absorption of the first order, but that a second-order absorption would be manifested by them.

If, on the other hand, the electronic configuration in the crystal is such that the midpoints between every pair of adjacent carbon atoms are *not* centres of symmetry, an oscillation of the two sets of atoms in opposite phases with respect to each other would give rise to a periodic displacement of the negative electric charges with the same frequency. The principal mode of free vibration of the structure having the highest frequency would accordingly manifest itself as a first-order absorption frequency. Thus, the presence of a first-order absorption would reveal that the crystal lacks centres of symmetry in its inner structure and hence should be assigned to the tetrahedral class of the cubic system instead of the octahedral or highest class of symmetry of that system. Since such lack of centro-symmetry is a consequence of the dynamic characters of the electronic configuration and not of any lack of symmetry in the static distribution of electric charge, the resulting first-order absorption cannot be expected to manifest the extraordinary strength with which it appears in such cases as, for example, the alkali halides. Indeed, it should not surprise us to find that the first and second-order absorption spectra of the diamonds exhibiting both of them are of comparable strength, instead of the first-order absorption being enormously more intense than the second-order as in the case of the alkali halides.

A few further remarks are here necessary. For the same reason that the first-order and second-order infra-red absorptions are of comparable strengths with the diamonds exhibiting both of them, we should expect to find that the characters of their second-order absorption spectra do not sensibly differ from those observed with the diamonds which exhibit only the second-order absorption. For, the origin of the second-order absorption would in both cases be the same, viz., the finiteness of the amplitudes of oscillation and the resulting incomplete cancellation of the displacements of electric charge of opposite sign in the alternate layers of the structure. Such cancellation would however continue to be operative in the first approximation even in the case of diamonds lacking centres of symmetry. The excitation of the principal mode of vibration having the highest frequency may, however, be expected to result also in the excitation of the modes of lower frequency as an accompaniment, the strength of such excitation being determined by the difference between their frequencies and that of the mode of highest frequency. In other words, in the first-order absorption spectrum of the diamonds exhibiting it, not alone the mode of highest frequency but also the modes of lower frequencies may be expected to appear, their strength falling off rapidly as the frequency deviates more and more from the highest.

Concluding remarks

Figures 1 and 2 above are reproductions of a selection from amongst the numerous spectro-photometer records illustrating the memoir cited above. They represent two typical cases and serve to show that the resemblances and differences between the absorption spectra of diamonds having the lower and the higher symmetries as observed are fully in accord with those indicated by the considerations set forth above. Attention may also be drawn to the extreme sharpness of the peaks of absorption as recorded by the spectrophotometer in both figures. Such sharpness is a natural consequence of the free vibrations of the structure of diamond exhibiting a set of nine precisely defined monochromatic frequencies. It should also be remarked that the frequencies determined spectroscopically as well as their observed activities are in satisfactory accord with those deduced theoretically. Further on the basis of the spectroscopically determined frequencies alone and without using any other data, the heat capacity of diamond can be evaluated theoretically over the entire range from the lowest to the highest temperatures: the results obtained are in highly satisfactory agreement with the thermally determined values. The reader will find these and many other matters set out and discussed in the memoir cited.

The diamond: Its structure and properties

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ABSTRACT

A critical study of the crystal forms of diamond from various sources demonstrates that the symmetry of the structure may be either that of Class 32 or Class 31, in other words that the structure may be either centrosymmetric or non-centrosymmetric. Diamonds belonging to Class 31 may however exhibit a pseudo-octahedral symmetry of external form by reason of the interpenetration of oppositely directed structures having the lower symmetry. The existence of diamond with two differing structures provides an insight into the many remarkable properties of this material, viz., the striking differences observed in the infra-red absorption spectra, differences in transparency to ultra-violet rays, the differences in the intensity of their X-ray reflections and the variations in the intensity and colour of the luminescence exhibited by them.

The modes of atomic vibration in diamond can be completely described and their frequencies evaluated by very simple procedures. The vibration frequencies can be determined experimentally by observations of the frequency shifts in the scattering of light or by infra-red spectroscopy, the results by the two methods being fully in agreement. The heat capacity of diamond may then be computed, giving results in highly satisfactory concordance with the observational data.

The principal mode of atomic vibration having a frequency of 1332 cm^{-1} is triply degenerate. These vibrations can be excited in the lattice planes of diamond by the incidence of monochromatic X-rays if it belongs to crystal Class 31. The three-fold degeneracy of the vibration reveals itself as the three distinct spots in the resulting dynamic X-ray reflection by the octahedral lattice planes.

The complete electronic frequency spectrum of diamond has been evaluated by a very simple procedure. The results are highly successful in explaining the known optical and spectroscopic properties of diamond.

1. The crystal forms of diamond

Geometric crystallography derives its significance from the fact that the external form of a crystal discloses the symmetry characters of its internal structure and that these characters are in their turn closely related to the physical properties of the solid. The study of the crystal forms of diamond thereby becomes a highly important first step towards an understanding of its many remarkable properties. It is a characteristic feature of diamond that it is generally found as single complete crystals which are bounded on all sides by the natural faces. The extreme hardness of the material also enables it to preserve its original shape undamaged through many vicissitudes, so much so that specimens taken out of secondary geological formations usually exhibit the natural faces of the crystal

with an undiminished brilliancy and lustre. These circumstances make the study of the crystal forms of diamond a highly rewarding pursuit.

As is well known, diamond belongs to the cubic system of crystals. There are five distinct classes in that system of which we are concerned here only with two, viz., those which in the usual system of numbering are referred to respectively as Class 31 and Class 32. The symmetry properties of Class 31 are the same as those exhibited by the geometric figure of a regular tetrahedron, while those of Class 32 similarly correspond to the symmetry of form of a perfect cube. Both of the classes possess six diagonal planes of symmetry, while Class 32 possesses in addition three axial planes of symmetry and a centre of symmetry. These additional features are not exhibited by Class 31.

In numerous cases, crystals of diamond of gem quality exhibit curved faces. In some diamonds one observes both plane and crystal faces in combination. There are also others which show plane faces almost exclusively. These circumstances have in the past led to much confusion and misunderstanding regarding the symmetry of the internal architecture of diamond and its relation to its external form. These difficulties however disappear if the following method of approach to the subject is adopted.

If the six diagonal planes of symmetry which are common to both Class 31 and 32 are drawn in space so that they intersect each other at some common point, and we then draw a closed surface around that point, it will be found that the surface appears divided up into 24 sectors. In the pattern thus formed on the surface, six points appear at which the diagonal planes of symmetry intersect each other in pairs, while at eight other points three of the planes intersect each other. The six points are the projections of the mid-points of the six faces of a cube, while the eight other points are the projections of the eight cube corners. If, besides the six diagonal planes of symmetry, we had also drawn the three axial planes of symmetry in their proper setting, the entire surface would have appeared divided up into 48 sectors, six of these sectors being found in each of the eight octants into which the surface would be divided up by the three mutually perpendicular axial symmetry planes.

Diamonds having only curved surfaces exhibit very varied shapes, but they all have certain features in common, namely that the exterior surface is not a single continuous sheet but is broken up into distinct areas by a pattern of sharply defined edges. This pattern exhibits the features referred to above appearing on a closed surface intersected by the six planes of diagonal symmetry of a cube. But we do not observe the features which would arise if the three axial planes of symmetry had been present. Thus, the externally observed features justify us in recognising such diamonds as crystals belonging to Class 31 and inferring from the absence of the features which distinguish Class 32 that they do not belong to Class 32.

On the other hand, the octahedron is the form which distinguishes Class 32 from Class 31 of the cubic system. Hence, if a diamond exhibits the form of a

regular octahedron with plane faces and sharp straight edges, we have of necessity to recognise it as belonging to Class 32 of the cubic system and not to Class 31. Diamonds exhibiting this ideal form are not unknown. In particular, the author's collection of specimens includes some small crystals of octahedral form with lustrous plane faces bounded by sharp edges. Such specimens demonstrate beyond all possible doubt that the crystal symmetry of diamond may also be that of Class 32.

The conclusion thus arrived at, viz., that some diamonds belong to Class 31 of the cubic system and that other diamonds belong to Class 32 of that system is of the highest importance. It is indeed the clue to the understanding of many remarkable properties exhibited by diamond. Before we pass on to consider the subject of the crystal structure of diamond, it will be useful here to discuss its observed crystal forms a little more fully.

It is noteworthy that crystallographers and mineralogists have in the past been unanimous in assigning diamond to the tetrahedral class of the cubic system, in other words to Class 31. They were led to make this assignment by a study of the observed crystal forms. The appearance of simple tetrahedra with plane faces and of rounded forms exhibiting the general shape of a tetrahedron clearly indicated the lower symmetry. Further, octahedra with plane faces often exhibited notches or grooves along their edges which could be interpreted as the result of the twinning of oppositely directed tetrahedral forms. A particularly interesting case of this kind is that in which the octahedral faces are not triangular in shape but have a well-defined hexagonal outline, and all the edges of the octahedron are replaced by depressions bounded by these hexagons, each depression exhibiting four faces which intersect along sharply defined edges. The author's collection of diamonds includes a specimen from South Africa showing these features. An inspection of it makes it evident that the diamond is an interpenetration twin of two hexaxis-tetrahedra.

India was the original home of the great diamonds which found their way to other parts of the world and helped to spread the fame of this gemstone. At the present time, diamonds are still forthcoming at and near Panna in Central India. Two visits to Panna made by the author many years ago gave him the opportunity of inspecting numerous specimens of the diamonds found in that area in their original form as crystals. Particular mention should be made of the magnificent set of 52 uncut diamonds ranging in size from 25 carats down to 2 carats strung together into a necklace by a predecessor of the Maharaja of Panna. The beauty of the necklace arises from the lustre and shapeliness of the gemstones. The two visits to Panna also enabled the author to acquire for his collection a set of specimens for a more detailed study.

The external features exhibited by the Panna diamonds in the collection are highly instructive. They are of very varied sizes and shapes. Two of them present a close resemblance to octahedra in their general shape. But the octahedral edges are not seen and indeed there is not the slightest indication of their presence. On the

other hand, the edges along which the diagonal planes of symmetry meet the curved surface of the diamond are conspicuously visible. The six points where these planes intersect in pairs are located at the six vertices of the pseudo-octahedral form of the crystal, while the eight points at each of which three planes intersect appear at the centres of its eight curved faces. These features indicate that while the diamond has the inner symmetry of the tetrahedral class, its external form which mimics octahedral symmetry is the result of the interpenetration of oppositely directed tetrahedral forms within the diamond.

In some of the Panna diamonds, the lower or tetrahedral symmetry is much more obviously exhibited in the externally observed forms of the diamond than in others. There are also several specimens in which the external shape of the diamond resembles neither an octahedron nor a tetrahedron but is almost spherical in form. But in all cases the curved surfaces clearly exhibit the ridges where they are intersected by the six diagonal planes of symmetry of the tetrahedron.

2. The two types of diamond

The difference between the diamonds belonging respectively to Classes 32 and 31 in respect of their symmetry properties is the same as the difference between the geometric forms of a regular octahedron and a regular tetrahedron, viz., that the former possesses a centre of symmetry whereas the latter does not. In other words, the two kinds of diamond may be described as being respectively of the centrosymmetric and non-centrosymmetric types. Two physical tests for ascertaining whether the structure of diamond does or does not possess centres of symmetry may be suggested. One is whether diamond exhibits piezo-electric or pyro-electric behaviour. The other is the study of its behaviour in respect of the absorption of infra-red radiation. In regard to the former, it may be remarked that since diamond consists of atoms all of one kind, viz., carbon, which are linked together by covalent bonds, the possibility of detecting piezo-electric or pyro-electric behaviour is exceedingly remote and may indeed be safely left out of consideration. On the other hand, the infra-red behaviour of diamond is readily tested. It is most conveniently studied with polished cleavage plates of diamond. Many such plates, including some of large size, are included in the author's collection. Studies made with these plates and a recording infra-red spectrophotometer are described and discussed in the author's Memoir No. 129 entitled "The infra-red absorption by diamond and its significance". The reader is invited to study this memoir and examine the numerous figures and photographs reproduced in it. They show clearly that the existence of centrosymmetric and non-centrosymmetric types of diamonds inferred from the study of the crystal forms is amply confirmed by the results of infra-red spectroscopy.

It is a noteworthy fact that the diamonds which exhibit an absorption of infra-red radiation in the spectral region of the fundamental atomic vibration frequencies are those which are revealed to be perfect diamonds when examined by various tests. It is thereby made evident that the absorptive power for infra-red radiation which they exhibit is an inherent property ascribable to their possessing a non-centrosymmetric structure. It is also significant that those diamonds which do not exhibit any infra-red absorption in those spectral regions and hence by inference are of the centrosymmetric class nevertheless exhibit an absorption of the second and higher orders, in other words of the overtones of the fundamental vibrational modes. In respect of this second-order absorption, the non-centrosymmetric and the centrosymmetric diamonds exhibit a precisely similar behaviour. This is a further and independent proof that the difference in behaviour of the two types of diamonds is a consequence of differences in their crystal symmetry. What exactly is the nature of the structural difference between the centrosymmetric and non-centrosymmetric diamonds is a question which will be dealt with a little later. It may here be pointed out that the differences in the infra-red behaviour go hand in hand with differences of a striking nature in respect of other properties. In particular, the centrosymmetric diamonds are found to be non-luminescent under ultra-violet irradiation, whereas the non-centrosymmetric diamonds exhibit a readily observable luminescence. The centrosymmetric diamonds exhibit a high degree of transparency to the near ultra-violet region of the spectrum, whereas the non-centrosymmetric diamonds show a strong absorption in the same region. These relationships have been demonstrated by appropriate methods and illustrated in the Memoir No. 129 already mentioned.

3. Normal vibrations of crystal structures

A fundamental theorem in dynamics due to Lagrange states that the small vibrations of a system of connected particles may be expressed as a summation of a set of normal modes with precisely defined frequencies in each of which the particles of the system all move in the same or opposite phases and that the number of such modes is equal to the number of degrees of freedom of movement in the system. The theorem sets no limit to the number of particles contained in the system and it is obvious that it provides the correct approach to the subject of the dynamics of crystal lattices in its relation to the theory of the specific heats of crystals and of their spectroscopic behaviour. The simplicity of the crystal structure of diamond enables us on the basis of this definition of the normal modes of vibration of its structure to describe them fully and proceed to the evaluation of their frequencies. These topics are dealt with fully in parts VI, VII and VIII of Memoir No. 129 and the frequencies as computed and as observed in the records of infra-red absorption have been compared with each other.

It will suffice briefly to recall the findings. It emerges that the diamond has nine normal modes of atomic vibration, the principal mode of highest frequency being that in which the two interpenetrating lattices of carbon atoms of which the diamond is composed oscillate as units against each other. The other eight modes may be described as oscillations of the layers of carbon atoms present in the octahedral and cubic planes respectively, either normally or tangentially to themselves, and the adjacent layers being either in the same or in the opposite phases.

4. Spectral shifts in light scattering

The discovery made by the author in February 1928 that monochromatic light diffused in a crystal is accompanied by additional radiations of altered frequency provides an extremely simple and precise method of identifying the modes of atomic vibration in crystals. On the basis of this earliest observations, the author in his address to the Faraday Society at its Bristol meeting in September 1929 suggested that the more perfectly ordered is the atomic space-grouping in a crystal, the sharper would be the lines recorded as frequency shifts in its spectrum of light-scattering. A striking confirmation of this emerged from the observation made soon afterwards that even with a very small diamond, a very sharp and intense line with a frequency shift of 1332 wave-numbers per second is recorded. This frequency shift arises from the mode of vibration of the diamond structure with the highest frequency.

None of the other fundamental modes of vibration of the diamond structure can manifest itself as a frequency shift for the reason that the alternation of phase of the movement as we pass from each cell of the structure to the next would cancel out the effects to be expected. It would be possible, however, for the modes to manifest themselves as overtones with doubled frequency shifts or also as summational frequency shifts. The effects thus arising would naturally be extremely feeble. In practice, they would be overpowered by the spectrum of the luminescence of diamond which is simultaneously recorded. The efforts made to record the second-order spectrum of diamond in the scattering of light proved successful only when non-luminescent diamonds were available and use was made of the intense excitation provided by the $\lambda 2537$ resonance-radiation of a water cooled magnet-controlled mercury lamp. The second-order spectrum of diamond as actually recorded in this manner exhibits features in excellent agreement with what is to be expected on the basis of the dynamic theory and other relevant considerations.

A very sharp line which is recorded at one end of the spectrum with a frequency shift of 2666 wave-numbers is clearly identifiable as the octave of the highest fundamental frequency of 1332 wave-numbers. Another line which stands out clearly near the other end of the spectrum with the frequency shift of 2176 is

clearly the octave of the frequency 1087 which is that of the oscillation of the cubic layers in the crystal normally to themselves. A strong band covers the range of frequency shifts from 2540 to 2450 and has a peak intensity at 2460. This arises from the superposition of the octaves and summation of the two frequencies 1273 and 1219, these being respectively the eight-fold and the six-fold degenerate oscillations tangential to themselves of the octahedral and cubic layers of atoms. The frequencies of 1176, 1010, 746 and 624 respectively are not recorded in the second-order spectrum of light-scattering.

The non-appearance of some of the vibrational modes and the observed relative strength of those which are actually recorded as octaves or summations in the second-order spectrum can be fully explained on the basis of the nature of the respective modes. It should be stated here that the spectrum of light-scattering and the spectrum of infra-red absorption do not differ noticeably in respect of the frequencies of the modes of vibration manifested therein. But the intensity relationships are altogether different in the two cases, as is indeed to be expected in view of the wholly different mechanisms involved.

5. The dynamic reflection of X-rays

Under the title "A new X-ray effect", the author with his assistant Nilakantan announced in the issue of *Current Science* for April 1940, the discovery of a highly remarkable phenomenon exhibited by diamond when a pencil of X-rays emitted by a copper target passes through it and the diffracted X-rays are recorded on a photographic plate. The specimen employed was a cleavage plate normal to the octahedral planes of the crystal. The diamond itself was of the type described earlier in this article as non-centrosymmetric, in other words, a diamond which does not give any sensible restoration of light when examined between crossed polaroids and displays infra-red activity both of the first and the second orders. The original publication of April 1940 was followed by several others in the *Proceedings of the Indian Academy of Sciences* in the years 1940 and 1941. Owing to unavoidable reasons, the subject was then laid aside and could be resumed only after many years when more powerful X-ray equipment became available. The results and conclusions then arrived at are set out in the author's Memoir No. 109 entitled "The diffraction of X-rays by diamond". Numerous illustrations of the phenomenon as observed in various settings of the crystal are reproduced in it.

Studies on the crystal perfection of the diamonds actually used in the work described in Memoir No. 109 were made by single crystal and double crystal X-ray spectroscopic methods. The results of the examination proved that they were absolutely perfect or ideal diamonds as is shown by their spectra which have been reproduced with the same memoir. It was further demonstrated by photographs appearing in the memoir that the X-ray diffraction effects observed exhibit the

same type of symmetry as the diamond itself; for example, the different sets of octahedral planes give identically similar results. Using a diamond which was a triangular twin, its two components show precisely similar effects turned round through 60° . It was thus firmly established that the effects under study were truly characteristic of the diamond crystal.

The importance of the studies described in Memoir No. 109 is that they demonstrate the effect discovered in the year 1940 to be a reflection of monochromatic X-rays by the lattice planes of the crystal with a small but quite definite change of frequency and that this X-ray effect is exactly analogous to the optical effect observed in the scattering of monochromatic light by diamond, with the difference that it is only exhibited by diamonds which are infra-red active in respect of the fundamental vibration of the frequency of 1332 wave-numbers, whereas the optical effect can be observed with all diamonds. The dynamical theory shows that this mode of vibration of the crystal structure of diamond is triply degenerate; in other words, it occurs along any of the three cubic axes of the crystal. This is beautifully confirmed by the fact that in appropriate settings of the diamond, the dynamic X-ray reflection by each octahedral plane appears as three well-separated spots: the reflections by other lattice planes show analogous effects in accord with the theoretical considerations developed in the memoir.

The possibility of observing the dynamic X-ray reflections by diamond arises because the mode of vibration of the structure which gives rise to them is highly monochromatic and repeats itself in the same fashion as we pass from cell to cell in the structure. Thus, the appearance of these reflections is itself a demonstration of the correctness of the approach to the dynamical theory of the atomic vibrations in diamond set out in Memoir No. 129.

6. The tetrahedral carbon atom

As has been described earlier, the study of the crystal forms of diamond leads us to conclude that there are two types of diamond of which the inner structures are respectively centrosymmetric and non-centrosymmetric. Actual observation shows that the diamonds of the centrosymmetric type exhibit the infra-red absorption of the second-order only, whereas diamonds of the non-centrosymmetric type exhibit both the first and second-order infra-red absorptions. Observation also shows that these same two types of diamond exhibit noteworthy differences in respect of their transmitting power for light appearing in the near ultra-violet part of the spectrum. Finally, we have the remarkable differences in the X-ray diffraction phenomena which they exhibit. Taking these facts into consideration, we are obliged to infer that we are here concerned with a fundamental difference in the symmetry characters of the binding of the carbon atoms within the crystal with each other.

Diamond may be very simply described as the result of two sets of carbon atoms holding each other in place, each atom of one set being surrounded by four others in a tetrahedral setting. The local symmetry at the centre of each carbon atom is only tetrahedral. What the symmetry of the structure is which results from the linking together of each carbon atom with four others depends on the nature of the linking. This question is fully discussed in the author's Memoir No. 104 entitled "The tetrahedral carbon atom and the structure of diamond". It has been shown that there are indeed alternative possibilities for the nature of the binding between the carbon atoms which do not involve any difference in the charges of the atoms, nor any difference in the energy of their binding.

The approach to the problem indicated in Memoir No. 104 enables us to understand why diamonds whose symmetry of structure is only tetrahedral may nevertheless succeed in exhibiting a pseudo-octahedral symmetry of form. The oppositely directed tetrahedral forms of the structure are indistinguishable from each other except in their geometric setting. Hence, they can freely intermingle with each other and the aggregate thus formed would tend to mimic octahedral symmetry to a greater or less extent. The aggregate would only be approximately but not absolutely homogeneous. The way is thus opened to a deeper understanding of various recondite properties of diamond, as we shall presently see.

7. The luminescence spectra of diamond

For a diamond to exhibit luminescence under ultra-violet irradiation, it is clearly necessary that it should be capable of absorbing the incident radiation. Diamonds of the non-centrosymmetric type exhibit a blue luminescence of which the intensity varies enormously with the specimen under study. Spectroscopic examination reveals that these diamonds exhibit an absorption band located near the violet end of the spectrum. Further, at exactly the same wavelength, an emission band appears in the spectrum of luminescence. A lowering of the temperature of diamond to -180°C results in a spectral sharpening of both the absorption and the emission with a shift towards shorter wavelengths. *Per contra*, raising the temperature of the diamond results in a great increase in their spectral widths. With the diamond held at -180°C , the sharpened line appears at $\lambda 4153$. This is accompanied in emission towards greater wavelengths and in absorption towards smaller wavelengths by a system of bands exhibiting an observable discrete structure. Measurements show that these bands owe their origin to the vibrations of the diamond structure accompanying the change in the electronic energy levels which manifests itself as the emission or absorption at $\lambda 4153$.

The enormous variations in the strength of the blue luminescence as between different diamonds is readily understood in terms of the non-homogeneity of structure due to the intermingling of the positive and negative tetrahedral forms

in the substance of the diamond. The greater the number of the discrete blocks in the aggregate, in other words, the greater is the mosaicity of the structure of the diamond, the more intense would be its luminescence and the stronger would be the associated absorption of light. This explanation is confirmed by the experimental result that the intensity of the ordinary X-ray reflections by the lattice planes increases *pari passu* with the intensity of its luminescence. The angular width of the reflection of monochromatic X-rays also increases in the same circumstances.

A second type of luminescence having a greenish-yellow colour is exhibited by many diamonds. Spectroscopic examination of this luminescence with the diamond held at a temperature of -180°C reveals that it arises from an emission band at $\lambda 5032$ accompanied by a vibrational band system at greater wavelengths. Likewise and in the same circumstances, these diamonds exhibit an absorption band at $\lambda 5032$ accompanied towards lesser wavelengths by vibrational bands. This type of luminescence is found to be exhibited by diamonds of the composite type, in other words, by diamonds in which both the centrosymmetric and the non-centrosymmetric are located in juxtaposition. In such cases, the luminescence is exhibited by the diamond as a set of parallel streaks over its area and not as continuously distributed within its volume. Photographs exhibiting these features have been reproduced in Memoir No. 129.

8. The electronic spectrum of diamond

Each of the carbon atoms in diamond has a shell of four electrons surrounding the nucleus. These electrons play the principal role in holding the atoms together in the ordered structure of the crystal. The atomic vibration frequencies are determined by the strength of such binding and by the masses of the atomic nuclei and they appear in the infra-red range of the spectrum. If, on the other hand, we assume the nuclei to be at rest and only the electrons to be disturbed from their positions of equilibrium, their oscillations would appear in the ultra-violet region. To evaluate the modes and frequencies of electronic vibration, we may proceed on the assumption that all four electrons in the shell behave as a single unit of which the mass is four times that of an electron, and that these shells oscillate around their positions of equilibrium in the same manner as the atomic nuclei in the vibrations of infra-red frequencies. The evaluation of the electronic spectrum of diamond then becomes a simple matter. We have only to multiply the infra-red frequencies by the square root of the ratio between the mass of a carbon atom and the mass of the four electrons taken together. The results of thus evaluating the electronic spectrum of diamond are shown in table 1.

The following results emerge from table 1. The electronic spectrum of diamond consists of a set of eight monochromatic frequencies which lie in the ultra-violet range. The highest frequency corresponds to the wavelength $\lambda 1010$ and the lowest frequency to the wavelength $\lambda 2157$. That this evaluation is highly

Table 1. Evaluation of electronic frequencies.

Mode	Degeneracy	Atomic vibration frequency (wave-numbers) cm^{-1}	Electronic spectrum (wavelengths) \AA
I	3	1332	1010
II	8	1273	1057
III	6	1219	1104
IV	4	1176	1144
V & VI	3 + 3	1087	1238
VII	4	1010	1332
VIII	6	746	1804
IX	8	624	2157

successful in describing the actual behaviour of diamond is evident. The cut-off wavelength for diamond in the ultra-violet is λ 2240, which is close to the greatest wavelength of λ 2157 appearing in table 1. The highest frequency represented by the wavelength λ 1010 would be that principally responsible for the optical dispersion of diamond, while the others of greater wavelengths would play only minor roles. This follows from the fact that only the mode of highest frequency repeats itself from cell to cell of the structure, while the others alternate in phase and their first-order effects would therefore cancel out. The refractive index of diamond in the spectral range extending from the red in the visible to the limit of transmission in the ultra-violet has been determined with great care by Peters. It is accurately represented by the formula given by him

$$(n^2 - 1) = \frac{\varepsilon_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{\varepsilon_2 \lambda^2}{\lambda^2 - \lambda_2^2}$$

where $\varepsilon_1 = 4.3356$, $\varepsilon_2 = 0.3306$, $\lambda_1 = 1060$ Angstroms and $\lambda_2 = 1750$ Angstroms. It will be seen that ε_1 is far larger than ε_2 and that the wavelength λ_1 is reasonably close to the smallest wavelength λ 1010 appearing in table 1. The difference between this wavelength and the wavelength λ 1060 which appears in the two-term dispersion formula of Peters may be explained as arising from the small contributions made by the adjoining modes of lower frequency listed in table 1. The formula fits the observed data of dispersion for both types of diamond in a very satisfactory manner.

9. The ultra-violet absorption spectra

The electronic spectrum of diamond as shown in table 1 consists of eight monochromatic wavelengths in the ultra-violet. But when the transmission of

ultra-violet radiation through a plate of diamond of the centrosymmetric type is examined, what is observed is a complete cut-off of the spectrum over the entire range of wavelengths covered by table 1. How is this discrepancy to be explained? We are assisted in finding the answer to this question by the fact that the wavelength at which the cut-off appears shifts with the temperature at which the diamond is held, altering from λ 2393 at 314° C to λ 2240 at -174° C. It is thereby made evident that the thermal agitation strongly influences the strength of the absorption by diamond. We have also to take note of the fact that the excitation of electronic vibrations by the incident radiation would be accompanied by the excitation of vibrations of the infra-red frequencies and of their overtones. In consequence, the frequencies at which absorption could occur would be very numerous and not eight only. Even at the temperature of liquid air, the thermal broadening of the electronic lines would not be negligible. Inevitably, therefore, the final result would be in the nature of a complete cut-off for any moderate thickness of the absorbing plate.

When the diamond is of the non-centrosymmetric type, there is a sensible absorption of wavelengths greater than λ 2240 instead of free transmission as in the case of the centrosymmetric diamonds. Much depends on the actual thickness of the plate of diamond with which the observations are made. A plate which has a thickness of only a tenth of a millimetre exhibits a sensible transmission for wavelengths less than λ 3000, the cut-off then being located at λ 2240 as in the case of diamonds of the other kind. But if the thickness is a few millimetres, there is practically complete extinction up to λ 3000. A noteworthy feature is manifested by these diamonds, viz., the appearance of a series of absorption maxima in the spectrum. By cooling the diamond to -180° C and by using diamonds of appropriate thickness, and a spectrograph of adequate resolving power and suitably regulating the exposures, it is possible to record and measure exactly the positions of as many as 25 distinct lines in the wavelength range between λ 3347 and λ 3015. Some of these lines are of considerable intensity, and others are less conspicuous. Further out in the ultra-violet between λ 2240 and λ 3015, it is possible to record and measure other absorption minima, the most conspicuous of them being the sharp doublet λ 2356–2360 and the doublet λ 2296–2298.

Two questions here arise calling for an answer. What is the origin of the absorption observed in the region of wavelengths greater than λ 2240, and why does its spectrum exhibit a series of sharply-defined lines? Further, why is this absorption exhibited only by diamonds having a non-centrosymmetric structure? In considering these questions, it should be remarked that there are no measurable differences in refractivity between the two types of diamond. It may be inferred from this that the electronic spectrum exhibited in table 1 is identical for both types of diamond and that the absorption frequencies manifested in the region under consideration make no sensible contribution to refractivity. A possible explanation of this situation is that these absorptions arise from the same set of electronic frequencies as those listed in table 1, but *diminished* by the

subtraction therefrom of the overtones of various orders of the infra-red frequencies. The subtractions would yield a series of discrete frequencies, the strength with which they are manifested decreasing rapidly in the higher orders. If the process of such absorption is regarded as involving a kind of infra-red activity, their non-appearance with centrosymmetric diamonds and their manifestation with diamonds of the other type becomes intelligible.

Before leaving this topic, we may remark that the manifestation of a whole series of sharp lines in the absorption spectrum of diamond is a convincing demonstration that the electronic spectrum of diamond is not continuous but exhibits a discrete and enumerable set of sharply-defined frequencies, capable of manifesting themselves as such in appropriate circumstances.

10. Thermal and thermo-optic behaviour of diamond

Utilizing the spectroscopically determined frequencies of atomic vibration with their respective degeneracies as listed in table 1, it is a simple matter to evaluate the heat-capacity of diamond over the entire range of temperatures from 0° to 1000° absolute. The Einstein functions multiplied by the respective degeneracies for each of the atomic vibration frequencies may be added up. We then add the contribution to the thermal energy made by the three omitted degrees of frequencies representing the translations of the atoms. The total is divided by 48. We thereby obtain a representation of the variation of specific heat with temperature which exhibits a very satisfactory agreement with the facts of observation. The calculations are fully set out in part X of the author's Memoir No. 129. It is, therefore, unnecessary to traverse the same ground here.

A remarkable property of diamond is that its refractive index increases with the temperature, indeed more and more rapidly as we proceed to higher temperatures. Studies of this phenomenon have shown it to be a consequence of the progressive fall with temperature of the characteristic dispersion frequencies of diamond. The characteristic frequencies in the infra-red also exhibit a similar fall which is also proportionately the same. This can readily be understood in view of the electronic and infra-red frequencies being related to each other as shown in table 1.

As an illustrative example, it may be mentioned that the principal vibration frequency which is 1333 cm^{-1} at -180° C falls to 1332 at 30° C , to 1327 at 320° C , to 1321 at 630° C , and to 1316 at 850° C . The corresponding frequency shift as observed in the spectrum of light scattering remains remarkably sharp over the whole of this temperature range.

Quantum theory and crystal physics*

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1. Introduction

The physics of the twentieth century differs fundamentally from the physics of the nineteenth mainly because of two theories known respectively as the Quantum Theory and the Theory of Relativity which form an integral part of its scheme of thought. It is these two theories that have enabled a far deeper understanding of the nature of the physical world to be attained than was possible at the end of the last century. One must here acknowledge the work of Albert Einstein who played the leading role in the development of both of these theories. His publications during the first two decades of the present century bear on every page the imprint of a powerful and penetrating intellect. Even after this lapse of years, the physicist of today will find the study of those papers a profitable and stimulating experience. Indeed, a good deal of what I have to say in this address only reflects the results of such a study in relation to the fundamental problems of the crystalline state of matter—a subject which has deeply interested me for several years past.

2. Origin of the quantum theory

The quantum theory arose from the attempt to explain the characters of the radiation which emerges from the window of an enclosed furnace heated to high temperatures. As is well known, the total intensity of such radiation increases rapidly with rise of temperature of the furnace. Simultaneously, there is a shift of the spectral maximum of intensity towards higher frequencies, as is indeed evident from the progressive change in colour of the radiation. Thermodynamic considerations indicate that this shift should occur in such a manner that the spectral frequency at the point of maximum intensity should be directly

* Presidential address to the Indian Academy of Sciences at Waltair on the 26th December 1956.

proportional to the absolute temperature of the furnace. Quantitative measurements confirm that this is the case and show that the changes in the intensity as well as in the spectral character of the radiation with rise of temperature agree with a formula for the spectral intensity in which the cube of the spectral frequency appears multiplied by an exponential function of a type made familiar by Boltzmann's well known principle. The argument of the exponential function is negative and has as its numerator the spectral frequency multiplied by one universal constant and as its denominator the absolute temperature multiplied by another universal constant. A small but important modification secures a much more satisfactory agreement between the formula and the facts of observation. In the modified expression, the exponential has the same argument with a positive sign and now appears in the denominator with unity subtracted from it. This is the celebrated Planck formula except for a multiplying numerical factor.

3. Einstein's derivation of the Planck formula

Einstein gave a physical interpretation of the Planck formula and also showed how the formula could be derived on the basis of simple physical considerations. He interpreted the formula to mean that radiation of all frequencies is emitted and absorbed by material bodies in discrete quanta of energy proportional to their respective frequencies. He also showed that the radiation formula follows very naturally if we assume that the energy of the material particle which emits the radiation is itself quantised, in other words, its energy of vibration alters by successive steps, each of which is equal to the quantum of radiation energy which is emitted in the process.

A more complete and logically satisfying derivation of the Planck radiation formula was given by Einstein ten years later, viz., in 1917. In that paper, the notion of probability which in the quantum theory replaces the determinism of the older physics finds a prominent place. Instead of assuming the radiator to be a harmonic oscillator as in his paper of 1907, Einstein dealt with the most general case of an oscillator which has a number of discrete energy levels. The probability of its being present in any one of them is expressed by the product of the inherent statistical weight characteristic of the level multiplied by the appropriate thermodynamic probability factor. The latter takes the form of an exponential function with a negative argument equal to the energy of the state divided by the product of the absolute temperature and the Boltzmann constant. Einstein then considers the probability of three different kinds of elementary processes occurring in any given small time interval. The first is a spontaneous transition from the higher to a lower state of energy with emission of radiation as contemplated in Bohr's theory of spectra; the second is a transition of the same nature but now induced by the presence of an external radiation field; the third is

a transition from the lower to the higher energy state also induced by the external field. The probabilities of the two latter transitions are taken as proportional to the energy density in the surrounding radiation field. A transfer of energy from the oscillator to the field and an absorption of energy from the field by the oscillator are involved respectively in the two processes. In a steady state of affairs, the probabilities of transition in the two opposite directions must necessarily balance each other. These considerations lead at once to the Planck radiation formula.

4. The crystal as an assembly of oscillators

The foregoing exposition of Einstein's original ideas is intended to furnish a theoretical background for a consideration of the fundamental properties of the solid state which is the subject of the present address. Elementary processes closely analogous to those contemplated in Einstein's paper of 1917 successfully describe the phenomena actually observed when a beam of monochromatic light traverses a crystal and the light diffused in its interior is examined spectroscopically. We observe in the spectrum of the scattered light sharply defined lines with frequencies both higher and lower than that of the incident radiation. The ratio of the intensities of each such pair of lines having equal spectral displacements in opposite directions is found to be expressed correctly by a Boltzmann factor corresponding to the change of frequency multiplied by Planck's constant, this again being multiplied by the fourth power of the ratio of the two spectral frequencies. These facts indicate that the displaced frequencies arise from transitions from a higher to a lower energy state and vice versa induced in the elementary oscillators comprised in the crystal by the incident radiation. We are thus naturally led to regard the crystal as an assembly of a great number of oscillators which form a system in thermodynamic equilibrium. The thermal energy of the crystal may then be equated to the sum of the thermal energies of all the oscillators of the different sorts of which it is composed.

It is evident from what has just been stated that the specific heats of crystals stand in the closest relation to their spectroscopic properties. The first step in the theoretical evaluation of the thermal energy of the crystal is accordingly to identify and enumerate the oscillators of which it is composed and to discover and specify the energy states which they can occupy.

5. The oscillators and their energy levels

To begin with, we may provisionally identify the oscillators with whose behaviour we are concerned with the groups of atoms present in the unit cells of the crystal structure. To discover the energy levels which these oscillators can

occupy, we may, at least in regard to the infra-red or vibrational levels, adopt the same procedure as that which has provided itself abundantly successful in the field of molecular spectroscopy. As is well known, that procedure consists in determining and enumerating the different possible modes of vibration in each one of which the atoms all vibrate with the same frequency and in the same or opposite phases.

In endeavouring to carry through the procedure indicated above, the difficulty immediately presents itself that the group of atoms present in any one unit cell of the crystal structure is not isolated but forms a connected system with the groups of atoms in the surrounding cells and these latter again are connected with groups of atoms further out and so forth. The mathematical and physical difficulties which present themselves by virtue of these interconnections disappear when we make use of the fundamental property of crystal structure, viz., that it comes into coincidence with itself following a unit translation along any one of its three axes. Hence any normal mode of vibration should also possess the same property, viz., it remains a normal mode following a unit translation of the crystal. This requirement immediately enables us to determine and enumerate the normal modes in the most general case of a crystal consisting of several interpenetrating Bravais lattices of equivalent atoms. It emerges that the normal modes are divisible into two classes; in the first class, the amplitudes as well as the phases of oscillation of equivalent atoms in adjoining cells of the lattice structure are identical, while in the second class of normal modes the amplitudes of equivalent atoms are the same but the phases are reversed along one or two or all three of the axes of the lattice. If the crystal consists of p interpenetrating Bravais lattices, there are $(3p - 3)$ normal modes of the first class and $21p$ modes of the second class.

Thus the result emerges that the vibrational energy levels of a crystal form a sharply defined set in much the same manner as the vibrational energy levels in the spectra of molecules. But this result would necessarily be modified when the effects of anharmonicity and the interactions of the different normal modes with each other are taken into consideration.

6. The spectroscopic behaviour of crystals

The theoretical results stated above are in complete agreement with the actual spectroscopic behaviour of crystals in the infra-red region of frequencies as revealed by diverse techniques of observation in appropriate physical conditions. For example, they furnish an immediate explanation of the spectroscopic effects exhibited by crystals in the scattering of monochromatic light as mentioned earlier. In some cases the energy levels are shown by the spectral shifts to exhibit a lack of sharpness. That this arises from the disturbing effects of anharmonicity is

demonstrated by cooling down the crystal to liquid air temperature. The energy levels then become perfectly sharp, as is to be expected. We need not dilate here upon the different techniques of spectroscopic observation which are available only in particular cases. Mention should be made, however, of the very general method of observing the energy levels in crystals by the techniques of infra-red absorption. These latter have been greatly improved of recent years and the results obtained with such improved techniques completely confirm the theoretical findings stated above.

A feature of special interest to which reference may be made here is in respect of the possibility of observing the $21p$ normal modes of the second class in which the phases of oscillation are opposed in adjoining cells of the crystal structure. It is to be expected that by reason of such opposition of phase these modes would be precluded from observation by any of the available methods of spectroscopic study. Fortunately, however, and for reasons which I shall not here dilate upon, this is not invariably so. The normal modes of the second class are actually accessible to observation in several cases and they then manifest themselves as discrete and sharply defined lines in the spectra, provided the effects of anharmonicity are either absent or else are suppressed by the use of adequately low temperatures. Their appearance is one of the most striking vindications of the correctness of the present theoretical approach.

7. The specific heats of crystals

Regarding a crystal as an assembly of an immense number of oscillators in thermodynamic equilibrium, the evaluation of its thermal energy as a function of the temperature reduces itself to the problem of classifying and enumerating the different sorts of oscillators comprised in it and determining the scheme of energy levels for the oscillators of each sort. An application of Boltzmann's principle then enables us to evaluate the average energy of an oscillator of that sort, and multiplying it by the number of such oscillators we obtain a sum total; the addition of the sums thus found for the different sets of oscillators give the total thermal energy of the crystal. By differentiating this total with respect to the temperature, we obtain the specific heat of the crystal.

As already stated, we have $(3p - 3)$ normal modes of vibration of the first kind and $21p$ normal modes of the second kind. Thus, we have $(24p - 3)$ modes and frequencies in all and these have equal statistical weight. They may be regarded as the internal modes of vibration of the $8p$ atoms contained in a volume element of the crystal whose dimensions are twice as large in each direction as the unit cell of the crystal structure. The three omitted degrees of freedom represented the translatory movements of these groups of $8p$ atoms each. If we leave the latter aside for a moment and also neglect the effects of anharmonicity, the specific heat of a crystal may be expressed very simply as the sum of $(24p - 3)$ Einstein

functions, each involving its own characteristic frequency; the total number of oscillators which contribute is the number of groups of $8p$ atoms each comprised in the crystal. To this sum must be added the contribution to the specific heat arising from the oscillations inside the crystal which are attributable to the translatory movements of these groups of $8p$ atoms each. In a paper which has appeared in the October issue of the *Proceedings* of the Academy, it has been shown how the latter contribution may be rigorously evaluated. The argument by which this is effected may be very simply stated. The translatory movements of the groups of $8p$ atoms each give rise to oscillatory movements in volume elements which comprise a still larger number of atoms. By taking a succession of volume elements of different sizes and taking note of the circumstance that the lower limit of frequencies of vibration thus arising would diminish in proportion to the increasing dimensions of the volume element, the spectral distribution of frequencies follows immediately. Their contribution to the thermal energy of the crystal is found to be expressible as an integral having a well known form involving Einstein's expression for the average thermal energy of a harmonic oscillator.

It may be mentioned in conclusion that the method sketched above has been successfully applied to the evaluation of the specific heats of crystals—including especially diamond and the metallic elements—down to the very lowest temperatures approaching absolute zero. The theory emerges triumphantly from the test.

8. Summary

The fundamental notions of quantum theory and thermodynamics indicate that a crystal should be regarded as an assembly of an immense number of oscillators whose energy states are quantised and which form a system in thermodynamic equilibrium. They also indicate that the spectroscopic properties and the thermal behaviour of crystals stand in the closest relation to each other. We are thus left with the problem of discovering and enumerating the oscillators of the different sorts comprised in the crystal and of determining their scheme of energy levels. This may be done by methods analogous to those which have proved successful in the field of molecular spectroscopy. The results obtained are in perfect agreement with the observed spectroscopic properties and thermal behaviour of crystals.

The specific heats of crystalline solids: Part I

SIR C V RAMAN

A correct appreciation of the nature of the thermal agitation in a crystal is obviously of fundamental importance in the physics of the solid state. Closely related to it is the problem of evaluating the heat content of a crystalline solid as a function of the temperature. These topics have formed the subject of some recent studies by the present writer. From them has emerged a theory of the specific heats of crystalline solids which is both simple and comprehensive and which succeeds in establishing a quantitative relationship between the thermal properties and the spectroscopic behaviour of crystals and accounts for the facts of observation in both of these fields. It accordingly seems opportune to offer a connected review of the subject in which the basic principles are set forth as simply and clearly as possible.

2. Some general considerations

A crystal is an assembly of great numbers of atoms (of the same or of several different species) in a three-dimensionally periodic array in space. Macroscopically regarded, a crystal of finite size is a single physical entity; and those problems concerning its physical behaviour in which the discrete atomic structure does not need to be specifically considered can be dealt with on that basis. But neither the evaluation of the thermal energy of the solid nor the determination of its spectroscopic behaviour is a problem of that nature. For, the discrete atomic structure of the solid is the very essence of both of these problems and it must therefore form the basis of any theoretical considerations regarding them. It is therefore a misconceived and irrational procedure to assume—as is done in the theories of Debye and Born—the macroscopic crystal to be itself the oscillating unit whose modes and frequencies of vibration determine the thermal properties and the spectroscopic behaviour of the solid. While we have necessarily to reject such an approach as inadmissible, we are also precluded from assuming that the individual atoms in the crystal are the oscillators with which we are concerned. This is obvious, for the atoms in a crystal are linked together by forces of a physico-chemical nature and hence they cannot oscillate independently of each other. Thus, when both of these extreme suppositions are laid aside, we are left with the following questions requiring an answer. What are the oscillators which

determine the thermal properties and the spectroscopic behaviour of a crystal? How are they to be enumerated, and in what manner are their modes and frequencies of vibration to be determined? The answers given to these questions stand at the very base of the problems now under consideration.

3. The normal modes of vibration

The fundamental theorem in classical mechanics regarding the small vibrations of a system of connected particles, taken in conjunction with the three-dimensional periodicity of structure characteristic of the crystalline state, furnishes us with the key to the solution of our problem. The theorem referred to states that the possible vibrations of the system are superpositions of a set of normal modes, in each of which the particles of the system (in the present case, the atoms) vibrate with the same frequency and in the same or opposite phases. Hence, any mode of vibration which satisfies this description and which can be regarded as a characteristic property of the crystal must also satisfy the further criterion that it remains the same when the crystal is given a unit translation along any one of the three axes of its structure. This can obviously happen in two ways: following the unit translation, equivalent atoms in the adjacent cell retain their amplitudes and phases of vibration unaltered, or alternatively, while the amplitudes remain the same, the phases are all reversed. Thus, we have $2 \times 2 \times 2$ or 8 different possible situations. If there are p atoms in each unit cell of the crystal structure, each of the 8 possible situations give us $3p$ solutions of the equations of motion of the p atoms in the unit cell, in other words, indicates $3p$ normal modes of vibration with their respective frequencies which can be regarded as characteristic of the structure of the crystal. Thus, in all, we have $24p$ solutions of the equations of motion which may be divided into three groups: $(3p - 3)$ normal modes in which equivalent atoms in adjacent cells oscillate with identical amplitudes and phases; $21p$ other normal modes in which the amplitudes of equivalent atoms in adjacent cells are the same but their phases alternate along one, two or all three of the axes of the crystal structure; and finally, the 3 excluded translations.

4. The oscillators and their enumeration

We proceed to consider the physical significance of the results deduced and stated above. What they indicate is that we shall not be justified in identifying the groups of p atoms each which form the units of the crystal structure as the "oscillators" in specific heat theory, since their juxtaposition in the ordered structure of the crystal results in an eight-fold increase in the number of distinct frequencies of internal vibration which these groups of p atoms each would possess if isolated

from each other. We have also to recognize the existence of additional modes of vibration within the crystal made possible by the translatory movements of the atomic groups as distinct from their internal vibrations. It is to be remarked, however, that the $(24p - 3)$ normal modes of vibration with discrete frequencies indicated by the theory can be regarded as the *internal* modes of vibration of the groups of $8p$ atoms each to be found in volume elements whose dimensions are twice as large in each direction as those of the unit cells of the crystal structure. If the entire crystal encloses N unit cells, the number of groups of $8p$ atoms included in it would be $N/8$. Multiplying this by $(24p - 3)$ which is the number of their internal modes of vibration, and adding to the product the number of degrees of the translatory freedom of movement of the same groups, we recover $3Np$, which is the total of the number of degrees of freedom of atomic movement in the crystal.

5. The vibration spectra of crystals

Thus, the atomistic approach to specific heat theory leads us directly to a result which is of fundamental importance in relation to the spectroscopic behaviour of crystals, namely, that by far the largest proportion of the atomic degrees of freedom of movement in crystals is manifested in their vibration spectra as a set of discrete monochromatic frequencies $(24p - 3)$ in number, p being the number of atoms in the unit cell, only the three omitted translations manifesting themselves in what may be designated as the “residual spectrum” comprising the lowest frequencies of vibration and having a different character which we shall consider presently. The nature of the vibration spectrum of a crystal as stated above which is indicated by the theory might have been anticipated *a priori* on general grounds. For, a crystal comprises within itself an immense number of similar and similarly situated groups of atoms which would necessarily be of identical dynamical behaviour. Hence, the modes and frequencies of internal vibration of these groups would all be the same and would be a characteristic property of the crystal. The reason why we have $(24p - 3)$ discrete frequencies and not $(3p - 3)$ is also readily understood. The additional $21p$ frequencies arise because of the coupling of the oscillators located along each of the axes of the structure, an effect analogous to that observed in the simple case of two similar oscillators which when coupled to each other exhibit two distinct frequencies of vibration instead of only one.

We must now consider the nature of the “residual spectrum” briefly alluded to above. This spectrum embodies the oscillatory movements arising from the *translations* of volume elements of the crystal each containing $8p$ atoms; they may be described as *internal vibrations* in volume elements of still larger size and therefore having lower frequencies. The frequency ν of such a vibration can evidently range from a lower limit $\nu = 0$ to the upper limit $\nu = \nu_L$, ν_L being the lowest of the $(24p - 3)$ discrete frequencies of atomic vibration. The manner in

which the disposable $3N/8$ degrees of freedom would be distributed over this range of frequencies can be deduced by a very simple argument. The total number of volume elements of an specified dimensions included in the crystal, and therefore also the number of degrees of freedom represented by their *translations* would diminish in inverse proportion to the cube of their linear dimensions, while the frequencies of their *internal vibrations* would vary inversely as the first power of the same. Hence the number of degrees of freedom appearing in the residual spectrum in the range of frequencies between 0 and ν would be proportional to ν^3 . By differentiation, we obtain the result that the number of degrees of freedom appearing between frequencies ν and $\nu + d\nu$, in other words, the number of oscillators in the crystal having frequencies in that range, would be $3N/8 \times 3\nu^2 d\nu/\nu_L^3$.

6. Quantisation of the vibrational energy

In his classic paper of 1907 introducing the quantum theory of specific heats, Einstein showed that the acceptance of his theory of light quanta inevitably leads to the conclusion that the energy of the mechanical vibration of elementary oscillators—such as the molecules of a gas or the structural units in a crystal—would also be related to their respective frequencies by the quantum rules. He also indicated a procedure by which the thermal energy of a crystal could be evaluated as a function of the temperature on the basis of the quantum hypothesis. He identified the thermal energy of the crystal with the energy of mechanical vibration of an immense number of *individual* oscillators distributed over its volume. It was assumed that these oscillators could be grouped into sets, each set comprising a great number of individual oscillators characterised by a common frequency of vibration. The total number of the oscillators of all kinds was taken to be equal to thrice the number of the atoms comprised in the crystal. The oscillators themselves were assumed to be harmonic and to occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The thermodynamic principle of Boltzmann was then introduced, leading to the result that the numbers of the oscillators occupying the various permitted levels are in the relative proportions indicated by that principle, and determined by the respective energies and by the temperature. The average energy of the oscillators in each of the sets was then evaluated. Summing up over all the oscillators in each of the sets and then over all the sets, Einstein obtained an explicit formula for the thermal energy of a crystal as a function of the temperature.

Einstein's ideas necessarily form the basis of any rational approach to the solution of the specific heat problem for crystals. For, they are based on an atomistic approach to the problem and effect a synthesis of the results of classical dynamics with the notions of the quantum theory and the basic principles of thermodynamics, in other words, of all the three disciplines which find a place in

the problem Einstein's formulation, however, had the weakness that he left unanswered three important questions: What precisely are the individual oscillators contemplated in the theory? How are they to be enumerated? How should their frequencies of vibration be determined? Also to enable his theory to be applied in the particular case of diamond, Einstein assumed that the individual atoms in that crystal were themselves the oscillators contemplated in his theory. This was an oversimplification which resulted in discrediting Einstein's theory. For, that assumption was theoretically unsustainable and it also led to values for the specific heats at low temperatures which were in disagreement with the experimental facts elicited by later investigations. It is not surprising in these circumstances that Einstein's approach to the specific heat problem was laid aside, and that other and totally different ways of approaching the same problem gained general acceptance.

The present approach to specific heat theory is in a sense a rehabilitation of Einstein's original ideas. It fills in the lacunae left by him and we are thereby enabled to make use of Einstein's formulae just as they stand for an evaluation of the thermal energy of the crystal. But, before we proceed to write down the expressions, it appears desirable to emphasize certain fundamental aspects of Einstein's theory which also find a place in the present approach to the subject. Einstein's application of Boltzmann's statistical-thermodynamical principle finds its logical justification in the fact that the crystal is regarded as an assembly of great numbers of similar oscillators capable of exchanging energy with each other and forming a system in thermodynamic equilibrium. The use of the principle implies that the energy of vibration of the individual oscillators of each sort exhibits fluctuations over the volume of the crystal both in space and in time, the magnitude of these fluctuations being naturally the greater, the higher the frequency of the oscillator considered. This picture of the thermal agitation in crystals is fundamentally in accord with the actual facts of crystal architecture as well as with the principles of thermodynamics, but it is very remote indeed from any ideas of its nature based on the notions of macroscopic physics.

Another feature of Einstein's theory which he himself stressed is the intimate relationship which it indicates between the thermal properties and the spectroscopic behaviour of crystals. The same relationship is also a feature of the present theory. But, the latter goes further than Einstein's, since it specifies the number of sets of oscillators which are the carriers of the thermal energy and also indicates the procedure by which their frequencies may be evaluated. Properties descriptive of the macroscopic behaviour of solids, viz., their elastic constants, do not as such find a place in the present theory of the specific heats of crystals.

7. Evaluation of the specific heats of crystals

Making use of the reasoning employed by Einstein, we obtain the following expression for the heat content of a volume of a crystal containing N unit cells of

the crystal structure as a function of the temperature, namely

$$\frac{N}{8} \left[\sum_{i=1}^{24p-3} \frac{hv_i}{\exp(hv_i/KT) - 1} + \frac{3}{v_L^3} \int_0^{v_L} \frac{3hv^3 dv}{\exp(hv/KT) - 1} \right].$$

The numerical factor 1/8 appears in the expression because each oscillator comprises 8 unit cells of the crystal structure. On differentiating the expression with respect to T , we obtain the formula for the specific heat.

The following remarks may be made regarding the numerical evaluation of the expression given above. All the $(24p - 3)$ frequencies would be distinct from each other only in the case of a completely anisotropic crystal. If any symmetry elements are present, the number of distinct frequencies would be naturally diminished, but the formula remains the same. Such reduction in the number of distinct frequencies would appear both in respect of the $(3p - 3)$ frequencies in which both the amplitudes and the phases are the same in adjacent unit cells and in the $21p$ others in which the phases may be opposite, as already explained. As an illustration of these remarks, we may consider a case in which $p = 2$ and the crystal belongs to the cubic class and its structure consists of two interpenetrating face-centred cubic lattices. The $(3p - 3)$ distinct frequencies then reduce to a single triply degenerate frequency; the $21p$ or 42 other vibrations reduce to only eight distinct frequencies, the modes relating to all of which may be readily described in geometric terms connected with the structure of the crystal.

Since the first term in the expression for the thermal energy is a summation extended over $(24p - 3)$ distinct modes of vibration, while the second represents the residual spectrum, it is evident that the latter would be of minor importance relatively to the first, especially in those cases where p is large, in other words when the crystal has a multi-atomic structure. The position is a little different when p is small, as for example, when p is equal to 1. The contribution from the second term would not then be altogether negligible in comparison with the first term. The second term also acquires some importance relatively to the first at very low temperatures. For, since the frequencies appearing in it are low, their contributions to the specific heat would survive when those due to the vibrations of the higher frequencies appearing in the first term have dropped out by reason of Boltzmann's principle.

The specific heats of crystalline solids: Part II

SIR C V RAMAN

The theory of the specific heats of crystals expounded in the first part of this review is similar in its approach to that originally proposed by Einstein in the year 1907, but it fills up the lacunae left in that theory and succeeds in connecting the thermal energy of crystals with their spectroscopic behaviour, as also in explaining the facts of observation in both of these fields. It is hoped on some later occasion to set out the results following from the theory in greater detail and to illustrate them by specific examples. The present review will conclude with some comments on the theory of the specific heats of crystals put forward by Debye in the year 1912 and the closely analogous theory published by Born and Karman at about the same time. A whole generation of physicists and chemists has been persuaded to believe that these theories embody valid physico-mathematical thought and that they satisfactorily account for the facts of observation. These are circumstances which justify the inclusion in the present review of some critical remarks on those theories.

2. The fundamentals of specific heat theory

We may usefully commence our examination by recalling the ideas embodied in Einstein's paper of 1907 in the form of three distinct propositions.

- I. A crystal is an assembly in thermodynamic equilibrium of an immense number of individual oscillators which are divisible into sets, each set consisting of a great number of oscillators characterised by a common frequency of vibration.
- II. The total number of oscillators of all sorts is equal to thrice the number of atoms comprised in the crystal.
- III. The vibrational energy of each individual oscillator is quantised and its average value taken over its different possible energy states may be determined by the aid of Boltzmann's principle.

The first of these propositions finds its justification in the known physical features of crystal architecture. The second proposition follows as a logical deduction from the first taken in conjunction with the results of classical mechanics. The third proposition is a logical consequence of the principles of thermodynamics and the quantum theory when applied to the circumstances

stated in the first proposition. In the earlier part of the review, it has already been shown how these propositions enable us to deduce both the thermal and the spectroscopic behaviour of crystals.

3. The theories of Debye and Born

The basic idea underlying these other theories is that the thermal energy of a crystal may be evaluated in the same manner as the energy density of thermal radiation within a perfectly reflecting enclosure, in other words, by summing up the kinetic and potential energies of sets of wave-trains which are assumed to fill the volume of the solid and form stationary wave-patterns in its interior. J H Jeans who was the original proposer of this idea indicated in his paper of 1909 a way of escape from the more obvious difficulties which arise when it is sought to make use of it. Debye and Born who derived their inspiration from Jeans naturally also took over from his paper the special assumptions needed to put his ideas into quantitative form. These special assumptions figure prominently in both of the theories and are indeed their most characteristic feature.

The stationary wave-patterns considered by Debye were those contemplated in the classical theory of elasticity for a solid of finite volume. An enumeration on the basis of that theory shows the total number of modes of vibration to increase—without any upper limit—proportionately to the cube of the frequency up to which the enumeration is carried. To enable the enumeration thus made to form the basis of specific heat theory, Debye assumed that the enumeration is valid only up to a certain upper limit of frequency and that no modes of vibration with higher frequencies exist; the upper limiting frequency was so chosen that the number of wave-patterns is equal in number to thrice the number of atoms comprised in the crystal.

The waves considered by Born are of a more general type than those considered in the Debye theory. Whereas Debye limited himself to the consideration of crystals of comparatively simple type, viz., those containing a single species of atom and belonging to the cubic system, the theory of Born accepts no such limitation and indeed claims to be applicable to all crystals. The special assumption which figures in the Born theory is the well known “cyclic postulate” which selects the permitted, wavelengths of the stationary wave-patterns filling the solid in such manner that the total number of wave-patterns is equal to thrice the number of atoms comprised in the crystal.

The questions which arise and which need to be considered are the following: Are the approaches to specific heat theory briefly summarized above logically sustainable? Are the ideas on which they are based and the conclusions to which they lead compatible with the fundamental principles of classical mechanics, thermodynamics and the quantum theory? We shall consider these questions and presently find that the answer is in each case definitely in the negative.

4. The logical fallacy

A simple calculation shows that the frequencies of vibration which determine the variation of the specific heats of crystals with temperature lie in the infra-red region of the spectrum. It follows that the oscillators which are the carriers of the thermal energy are the ultimate structural elements in the crystal. This is further confirmed by the fact that when the atoms are firmly bound together in the structural elements of the crystal, as is the case for example with diamond, the specific heats are low and the vibrational frequencies estimated from them are high; the latter inference receives direct support from spectroscopic studies. It follows from these remarks that the approach to the specific heat problem made in the theories of Debye and Born is totally misconceived. These authors concern themselves with an entirely different and irrelevant subject, namely, the vibrations of a macroscopic solid and proceed to determine and enumerate them, treating it as a boundary-value problem in wave-propagation. It is easily shown that the results thus obtained are wholly unrelated to the specific heat problem. We have only to recall that wave-motion is a kinematic concept. Hence the stationary wave-patterns inside an enclosure can be described in purely geometric terms without any reference to the question whether the material traversed by the waves does or does not possess a discrete structure. In other words, there is no nexus or connection between the stationary wave-patterns assumed to exist in the medium and the discrete structure, if any, which it possesses. It is not surprising in these circumstances that Debye and Born are obliged to introduce postulates into their theories which assume the existence of such a relationship. We have only to remark that such postulates or assumptions savour of sophistry and that theories embodying them can lay no claim to logical validity.

5. Falsity of the dynamical consequences

The theories of Debye and Born are attempts to carry over the ideas and methods of macroscopic physics into the fields of atomic dynamics, thermodynamics and quantum theory where they are inappropriate and indeed wholly out of place. The procedures they adopt naturally lead to consequences which are irreconcilable with the basic principles of these disciplines and the results following from them.

Considering the matter first from the stand-point of atomic dynamics, it is clear that we are not concerned here either with wave-propagation or with any boundary value problem. Specific heat theory rests on the determination and enumeration of the normal modes of vibration of the ultimate particles of the material, in other words, of the atoms present in the structure of the crystal. Since the range of the interatomic forces is limited and small compared with the

dimensions of any crystal of macroscopic size, these normal modes are determinable from the structure of the crystal without any reference to the size of the crystal or to the conditions at its external boundary. This also becomes evident when we compare the frequency of the atomic oscillations with the frequency of the elastic oscillations of a macroscopic crystal. The former is very great in comparison with the latter even for a crystal of colloidal dimensions. Hence the oscillations of the atoms in the interior of a crystal repeat themselves many thousands of times, thereby defining their frequency with all necessary precision, before any disturbance originating in the interior of the crystal could travel out to reach its surface and return after reflection to the place of its origin. Hence, whether the boundary is there or not makes no difference to the modes and frequencies of atomic vibration.

The fallacy of identifying the atomic vibrations with stationary wave-patterns is obvious even in such simple cases as those considered by Debye. The vast majority of the stationary wave-patterns assumed in his theory to be the carriers of the thermal energy of the crystal have wavelengths of the same order of magnitude as its lattice spacings. These are precisely the circumstances in which it is not permissible to identify the dynamical behaviour of a discrete structure with that of a medium of uniform density. The consequence of such identification is to endow the crystal with an immense number of modes of vibration with frequencies all different from each other throughout the range under consideration and thus to present a false picture of the spectroscopic behaviour of the crystal.

Though Born's theory nominally takes account of the discrete lattice structure of crystals, his "postulate of the cyclic lattice" is equivalent to assuming that the normal modes of vibration of the atoms are similar to the oscillations of the volume elements in a continuous solid having the same shape as the unit cell of the crystal but of greatly enlarged size. The stationary vibrations permitted by the postulate accordingly appear in immense numbers with wavelengths and frequencies all different from each other and with their modes wholly unrelated to the structure of the crystal. It is important to remark in this connection that Born does not restrict himself to simple lattice structures but also claims his theory to be valid for all crystals. Any one who appreciates the nature of the results following from Born's lattice theory will realize that the ideology behind his dynamics is completely false. In effect, Born endows the atoms in a crystal with a vast number of modes and frequencies of vibration which are wholly unrelated to its internal architecture and which have a continuous spectrum of frequencies, a result which is in flagrant contradiction with the facts of observation revealed by spectroscopic investigations.

6. Conflict with thermodynamics

A stationary wave-pattern is a mode of vibration in which all the volume elements of the medium oscillate with the same frequency and in the same or opposite phases and with relative amplitudes which remain invariant with time. Vibrations of this type are characteristic of a macroscopic solid and can be considered as its normal modes of vibration and determined by the methods of the classical theory of elasticity. Such vibrations can also be set up and maintained in an elastic solid artificially, as for example, by the use of a piezo-electric oscillator attached to it.

The identification of the thermal agitation in crystals with stationary wave-patterns of the nature described above which is postulated in the theories of Debye and Born is however clearly irreconcilable with the statistical concept of the nature of thermal energy in material bodies. Thermal agitation is envisaged in Boltzmann's entropy-probability principle as a chaotic and fluctuating disturbance varying in its character and intensity from instant to instant and from place to place within the material. Atomic groups of similar nature which are located in parts of the crystal not contiguous to each other may indeed vibrate with the same frequency. But there can be nothing in the nature of definite relationships either in their amplitudes or in their phases of vibration persisting in time.

The issue can also be put a little differently. A crystal is an assembly of an immense number of individual atoms which are capable of moving from their positions of equilibrium. Hence the state of the system can only be described in terms of the values of a very large number of independent variables. The interactions between neighbouring atoms would naturally influence their relative movements and determine their modes and frequencies of vibration. But we cannot in any circumstances regard the entire assembly as a single unit in the thermodynamic sense or postulate constancy of amplitude or coherence of phase in the atomic vibrations over its entire volume. A description of the thermal agitation in precisely defined terms is possible only for domains of space and periods of time which are small in comparison with macroscopic standards. In other words, the entire ideology behind the theories of Debye and Born is incompatible with the fundamental notions of the nature of thermal energy which lie at the base of the science of thermodynamics.

7. Misinterpretation of the quantum theory

As has been shown above, the theory of specific heats can be placed on a logically sustainable basis only if we recognize that the oscillators which are the carriers of the thermal energy are the structural elements in the crystal. We then obtain a picture of the thermal agitation in the solid which is consistent with the general

principles of dynamics and of thermodynamics. Necessarily, therefore, it is these same oscillators whose vibrational energies must be assumed to be quantised. Since, further, these oscillators are present in large numbers distributed over the volume of the crystal, we have a logical justification for the use of Boltzmann's principle in conjunction with the quantum hypothesis for the evaluation of the average energy of the oscillators of any particular frequency and therefrom also the evaluation of the heat capacity of the entire crystal.

To the fallacies which vitiate the Debye and Born theories we have therefore to add one more, viz., that they give a fantastic and altogether meaningless interpretation to the postulates of the quantum theory. They proceed to quantise the energy of the normal modes of vibration of a macroscopic crystal; in doing this, they ignore the fact that the theory of quanta possesses a meaning and significance only in relation to the behaviour of the physical entities which the language of determinism characteristic of macroscopic physics cannot successfully describe. For example, we can speak meaningfully of quantising the energies of rotation or vibration of a molecule of benzene; but it is patently absurd to quantise the vibrations of a tuning fork or the rotations of a flywheel.

The specific heats of some metallic elements— Part I. Analysis of the experimental data

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1. Introduction

It is proposed in this paper to analyze the data for the variation of the specific heat with temperature of some metallic elements. The method of analysis is that already explained and discussed in an earlier paper¹ in these *Proceedings* with reference to the specific heat data for diamond, viz., to determine, with the aid of a table of Einstein's specific heat function, the particular frequency of vibration which if assumed to be common to all the atomic oscillators would give for the specific heat of the substance the actual value observed at any given temperature. The frequency thus calculated is designated as the effective average frequency of the atomic oscillators for that substance at that particular temperature. It is itself a function of the temperature and a graph showing how it varies as we proceed from the highest to the lowest temperatures gives useful indications regarding the distribution of the atomic degrees of freedom of motion over the entire range of frequencies in the vibration spectrum.

The four metallic elements the data for which will be analyzed in this paper are aluminium, copper, silver and lead. They all crystallize in the cubic system in forms based on the so-called face-centred cubic lattice which is really a simple Bravais lattice with only one set of equivalent atoms occupying the corners of a rhombohedral unit cell. We shall make use of the data for the specific heats of these metals determined by Giaque and collaborators.² The four metals form a sequence in which the fall of the specific heat at constant volume from the maximum given by the Dulong–Petit formula manifests itself progressively at lower and lower temperatures. There is a special appropriateness in their choice for the present study, since it was the data for these four metals as well as the data for diamond determined by Nernst and Lindmann³ which were made use of by Debye⁴ in a well known paper as support for his theory of the specific heats of crystals.

2. The specific heat data

The specific heat data we make use of are plotted as the lower of the two graphs appearing in figures 1, 2, 3 and 4 which refer respectively to the four metals aluminium, copper, silver and lead. The absolute temperatures are entered on the scale of abscissae at the foot of each figure. The scale of ordinates for the specific heats in cal/gm atom/degree appears on the left-hand side of each figure. The specific heats observed are shown as dotted circles and fall on a smooth curve which touches the axis of abscissae at the lowest temperatures and tends to

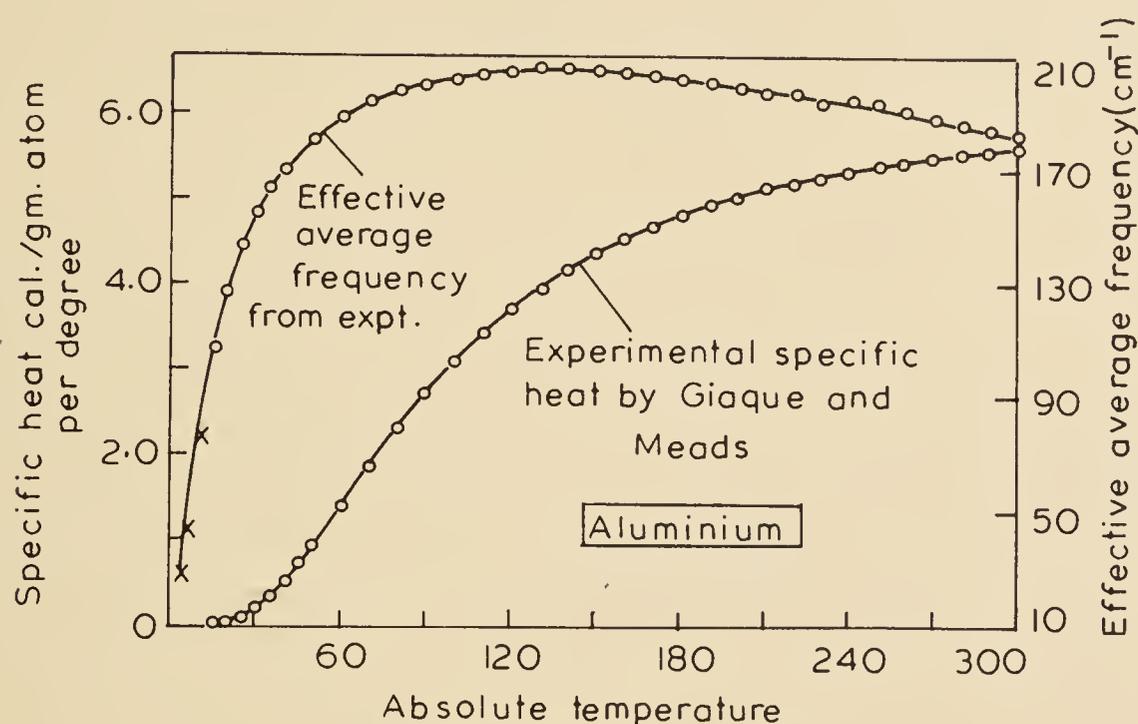


Figure 1. Analysis of the specific heat of aluminium.

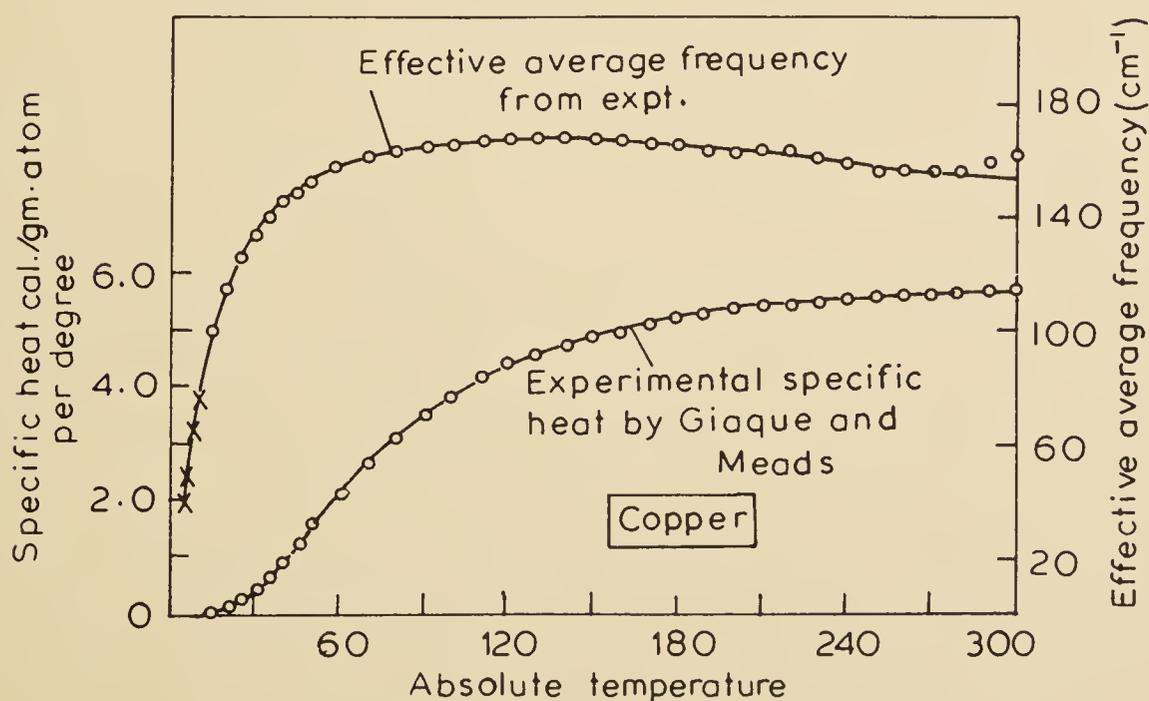


Figure 2. Analysis of the specific heat of copper.

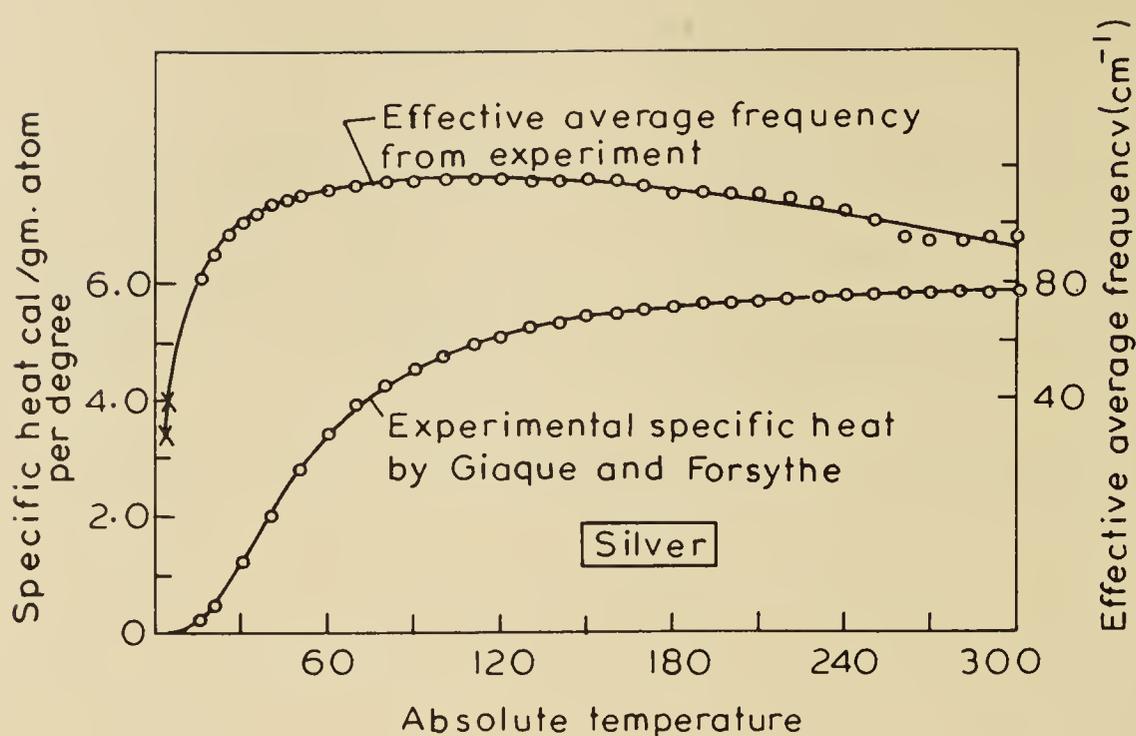


Figure 3. Analysis of the specific heat of silver.

approach the maximum limit at higher temperatures. The scale of ordinates used for the specific heats is rather too small for the values at the very lowest to be adequately represented. The slope of the specific heat curve at the upper end of the temperature range is greatest for aluminium, less for copper, still less for silver, while for lead it is almost indistinguishable from a horizontal straight line.

3. The effective average frequency

The upper of the two graphs in each of the four figures represents the average effective frequency of the atomic oscillators calculated in the manner already explained. The frequencies are shown in the usual spectroscopic nomenclature as wave-numbers and the scale of ordinates for the same appears on the right-hand side of each figure. The calculated values are shown as dotted circles and a smooth curve has been drawn through them. It will be seen that they exhibit a certain amount of scatter in the higher parts of the temperature range in each case. This is not surprising, since a very small error in the determination of the specific heat at this part of the range would represent a large error in the calculation of the effective average frequency. The graphs have been drawn as smooth curves to represent the general trend of the calculated values, ignoring the accidental fluctuations.

It appeared important to continue the graphs to still lower temperatures than those covered by determinations by Giaque and collaborators. Accordingly, we have made use of the data obtained by other authors⁵⁻⁷ for determining the effective average frequency of the atomic oscillators in this lowest part of the temperature range. The computed frequencies are shown as crosses on the

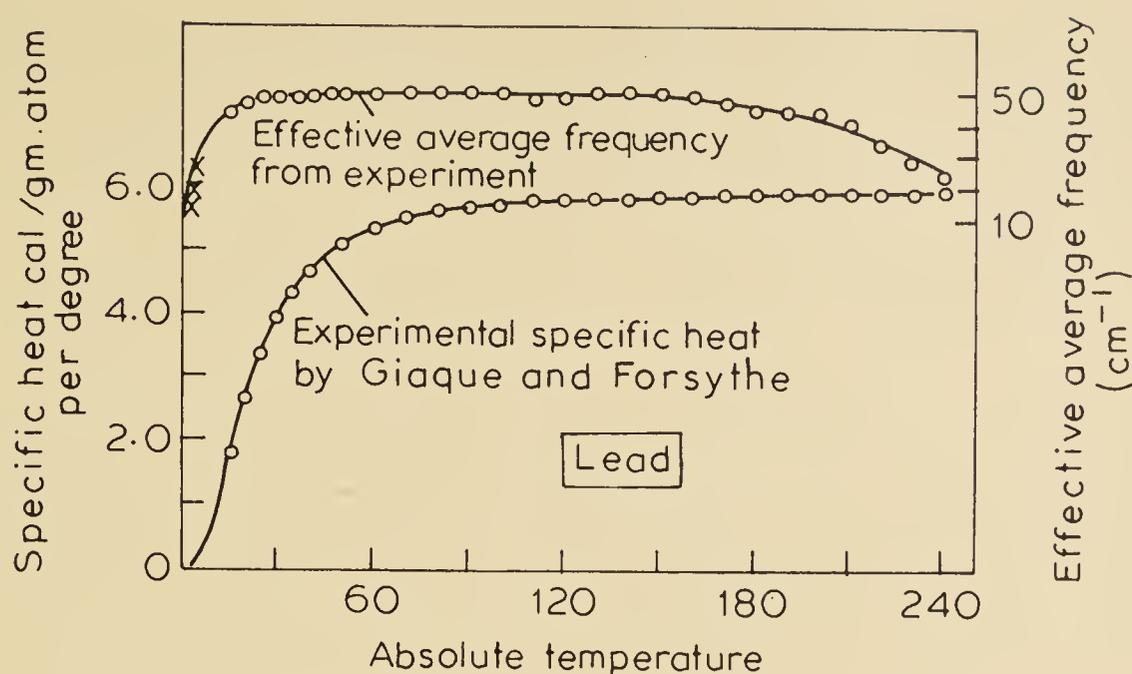


Figure 4. Analysis of the specific heat of lead.

extreme left-hand side of the figure in each case and the graphs have been prolonged so as to pass smoothly through those points.

4. The significance of the results

On a comparison of the frequency-temperature graphs for the four metals, it will be seen at once that while there are certain general similarities, there is also a progressive change in form as we go down the series. All the four curves show a maximum in the middle part of the temperature range covered by the data. This maximum can be located pretty definitely at about 135°K for aluminium. In the case of the other three metals, it becomes progressively more difficult to fix upon a definite temperature as the location of the maximum, the graph being practically a horizontal straight line over an increasingly larger range of temperatures. In other words, the effective average frequency of the oscillators has a practically constant value over a wide range of temperatures. This frequency (in wave-numbers) is 206 for aluminium, 167 for copper, 113 for silver and 50 for lead.

The shape of the graph at low temperatures recalls the course of the graph in the case of diamond already described and discussed in detail in the earlier paper already cited. It is sufficient here to remark that the progressively steeper fall of the graph to low frequencies with the fall of temperature is a consequence of the contribution to the specific heat made by the atomic vibrations of higher frequencies dropping out progressively, until finally at the lowest temperatures we are left only with the contribution made by the vibrations of the very lowest frequencies.

The horizontal stretch of the curves in the middle parts of the temperature range is very clearly analogous to that appearing in the case of diamond throughout the higher parts of the temperature range. Hence, as in the case of

diamond, we infer that in this region the effective average frequency of the atomic oscillators is the same or nearly the same as the arithmetical average of the atomic vibration frequencies, the latter term having the same significance as in the discussion of the data for diamond.

5. Frequency changes at the higher temperatures

We turn next to consider the course of the curve in the higher parts of the temperature range. We may reject any interpretation of the features which it exhibits as arising from errors in experimental data. For, the same phenomenon is shown by all the four metals in the same temperature range but to different extents, as is to be expected. Hence, the only possible interpretation of the drop in the effective average frequency at the higher temperatures shown by the graphs is that the atomic vibration frequencies are themselves a function of the temperature and progressively diminish as the temperature rises. It is not possible from the specific heat data to infer what the rate of such diminution is in the lower parts of the temperature range. But we can definitely infer from the form of the curves at the higher temperatures that the fall of the atomic vibration frequencies with rising temperature is at first rather slow, but that it accelerates and finally reaches a fairly steady rate at the higher temperatures.

The detailed discussion of the effects thus brought to light by our present analysis is more appropriately dealt with in part II of the present paper which concerns itself with the theoretical evaluation of the specific heats of metals as a function of temperature. We may, however, briefly record here some numerical results regarding the rate of fall of the atomic vibration frequencies (expressed as a fraction thereof per degree centigrade) which may be deduced from the slope of the graphs in the case of these four metals. As already remarked, this temperature coefficient is not a constant and we have therefore to consider its value in the vicinity of some temperature at which the graph has a fairly uniform slope. The values deduced in this way are given below in round figures, and represent the quantity $(1/\nu)(\Delta\nu/\Delta T)$, ν being the effective average frequency of the atomic oscillators. The figures for copper, silver and lead indicate a rather steep increase in the temperature coefficients of the atomic vibration frequencies with increasing atomic mass.

Substance	Atomic weight	Temperature	Temperature coefficient of frequency
Aluminium	27.0	255° K	10×10^{-4} per degree
Copper	63.6	250° K	6×10^{-4} „
Silver	107.9	270° K	21×10^{-4} „
Lead	207.2	215° K	99×10^{-4} „

6. Summary

The specific heat data in the temperature range from 15° to 300° reported by Giaque and collaborators for the four metals aluminium, copper, silver and lead are analysed and the effective average frequency of the atomic oscillators deduced therefrom is plotted as a function of the temperature. The graphs exhibit a steep fall of the effective frequency at very low temperatures as is to be expected. In the middle part of the temperature range, the frequency exhibits a broad maximum which in spectral wave-numbers is respectively 206, 167, 113 and 50 for the four metals. At higher temperatures the graph exhibits a second fall which indicates that there is a real and progressive diminution of the actual vibration frequencies of the atoms in the crystal with rising temperature in this range. The effect becomes increasingly more pronounced with increasing atomic mass.

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The specific heats of some metallic elements—Part II. Approximate theoretical evaluation

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1. Introduction

In this second paper of the series, we consider the problem of evaluating the specific heats of the four metals aluminium, copper, silver and lead, making use of the theoretical ideas set forth in an earlier paper in these *Proceedings*.¹ The metallic atoms in all these four cases are located at the equivalent points of a simple Bravais lattice of which the unit cell is a rhombohedron. Accordingly, all the normal modes of vibration are of the second kind, namely, those in which the successive atoms along one, two or all the three axes of the lattice oscillate with equal amplitudes but with opposite phases. By simple inspection of a model of the structure, it can be seen that the twenty-one possible normal modes of this kind group themselves into only four distinct modes with 3, 6, 4 and 8 as their respective degeneracies. These may be described in simple geometric terms: oscillations of the atoms in the cubic planes along the normals to those planes (degeneracy 3); oscillations of the atoms in the cubic planes tangential to those planes (degeneracy 6); oscillations of the atoms in the octahedral planes normal to those planes (degeneracy 4); oscillations of the atoms in the octahedral planes tangential to those planes (degeneracy 8). Accordingly, the specific heat of these metals is obtained by a summation of the Einstein functions for the frequencies of these four modes multiplied by their respective degeneracies. To this must be added the contribution arising from the spectrum of vibrational frequencies with a statistical weight of three arising from the three translations of the unit cell with the 8 atoms at its corners. This contribution appears as an integration of Einstein functions taken over a continuous spectrum of frequencies, the upper limit of frequency in the integration being the lowest of the four characteristic frequencies.

2. Evaluation of the characteristic frequencies

Each of the atoms in a face-centred cubic lattice has twelve nearest neighbours, six second neighbours, twenty-four third neighbours and twelve fourth neigh-

bours. The six constants needed to determine the force on any one atom resulting from the displacement of another atom reduce, by virtue of the symmetry of the structure, to *three* constants in the case of the nearest neighbours, *two* constants for the second neighbours, *four* constants for the third neighbours and so on. Thus, even if only the first three sets of neighbours are considered, the equations of motion of an atom would involve nine force-constants arising from the displacements of the surrounding atoms. In the absence of any knowledge regarding the magnitudes of these nine constants, it is not possible to evaluate the four frequencies which we need to know. In the case of diamond dealt with in an earlier paper in the *Proceedings*, it was possible to proceed on the basis of its known spectroscopic behaviour and to make an independent evaluation of the eight characteristic frequencies of vibration of its structure. It is obvious that a different procedure has to be adopted in the case of the metallic elements.

What we have to ascertain are the frequencies of vibration of the atomic *layers* lying respectively in the cubic and octahedral planes normally or tangentially to themselves. It is evident that the frequencies of such vibration would depend on the integrated effect on any one *layer* of the movements of the neighbouring layers. Various considerations indicate that the force acting on any layer would be determined *principally by the displacements relatively to that layer of the two neighbouring layers lying one on either side of it*. By way of justifying this statement, we remark that the first, second and third neighbours of any one atom are mostly to be found either in the same layer or in the two adjacent layers. For instance, in the cubic layers all the twelve near neighbours, four out of the six second neighbours and sixteen out of the twenty-four third neighbours are to be found thus located. Likewise, in the octahedral layers all the twelve near neighbours, all the six second nearest neighbours and eighteen out of the twenty-four third neighbours are to be found thus located. Hence, the frequencies of oscillation with which we are concerned may *as a first approximation* be evaluated on the basis that the forces on any one layer arise only from the displacements relative to it of the two neighbouring layers, one on either side of it.

For the same reasons as those explained above, the forces which determine the velocities of elastic wave propagation in the cubic and octahedral directions would likewise be determined *as a first approximation* by the displacements relative to any layer of the two neighbouring layers one on either side. Hence, we are in a position to establish simple but approximate relationships between the characteristic frequencies of vibration of the lattice and the velocities of propagation of elastic waves (longitudinal or transverse as the case may be) in the directions normal to the cubic and octahedral planes respectively. This relation may be written as below:

$$\text{Characteristic frequency} = \frac{2}{\pi} \cdot \frac{\text{Velocity of long elastic waves}}{\text{Twice the distance between adjacent layers}}$$

The correctness of the formula is easily verified by comparison with the case of

a simple linear lattice, viz., a string under tension loaded with identical mass-particles at equidistant intervals.

3. Numerical results

The foregoing approximate relationships between the velocity of propagation of elastic waves along the octahedral and cubic axes and the characteristic frequencies of a face-centred cubic lattice enable us to evaluate the latter for those crystals for which the elastic constants have been determined with precision. The published determinations make use of the three constants C_{11} , C_{12} and C_{44} contemplated in Voigt's theory. The four velocities we are concerned with are the square roots of C_{11}/ρ , C_{44}/ρ

$$(C_{11} + 2C_{12} + 4C_{44})/3\rho \quad \text{and} \quad (C_{11} - C_{12} + C_{44})/3\rho.$$

In the cases of aluminium² and copper,³ the values of C_{11} , C_{12} and C_{44} are available over a wide range of temperatures from the very lowest upwards. They exhibit a progressive diminution with temperature, which at first is slow but accelerates at high temperatures. In the cases of silver⁴ and lead,⁵ however, determinations of the elastic constants only at room temperatures are available and we shall make use of them.

Table 1. Characteristic frequencies in wave-numbers.

Mode	Degeneracy	Aluminium		Copper		Silver	Lead
I	3	353	340	260	255	179	88
II	6	177	169	177	171	109	48
III	4	287	302	269	263	179	87
IV	8	145	138	113	109	70	30
Average		211	207	182	177	117	54

Table 1 shows the four characteristic frequencies calculated in the manner explained above. In the cases of aluminium and copper, the values are given at absolute zero as also at room temperature, while in the case of silver and lead, only room temperature values are given. Multiplying the frequencies by the degeneracies of the respective modes, then adding up and dividing by 21, we get the arithmetical average of the four frequencies. This is shown at the foot of the table in each case.

As the elastic constants diminish with increasing temperature but not all in the same manner, it is not altogether surprising to find that one of the calculated frequencies for aluminium actually increases instead of diminishing with rise of

temperature. However, both for aluminium and for copper the arithmetical average shows a noticeable fall at room temperature as compared with the value at the absolute zero.

4. Calculation of the specific heats

The expression for the thermal energy of the crystal is given by the formula

$$\frac{N}{8} \left\{ \sum_{i=1}^{i=4} \frac{h\nu_i}{e^{h\nu_i/kT} - 1} + \frac{3}{v_4^3} \int_0^{v_4} \frac{h\nu}{e^{h\nu/kT} - 1} 3\nu^2 d\nu \right\},$$

where N is the number of lattice cells contained in the volume of the crystal under consideration. Differentiating this with respect to T , we obtain the specific heat of the crystal at any given temperature. In evaluating the same, we make use of the tabulated values of the well-known functions appearing in the expressions.

The values of the specific heat have been plotted as functions of the absolute temperature in the lower of the two graphs in figures 1, 2, 3 and 4 which refer respectively to the four metals. As usual, the abscissae are the absolute temperatures, and the scale of ordinates for the specific heat appears on the left-hand side of the figure in each case. The upper graph in each figure is the effective average frequency determined from the calculated specific heat in the manner already explained in the previous papers. The scale of ordinates for this frequency appears on the right-hand side of the figure in each case and is expressed in wave-numbers.

It will be noticed that at the upper end of the temperature range in each of the four cases, the effective average frequency of the atomic oscillators deduced from the calculated specific heats is respectively 210, 182, 117 and 55 cm^{-1} . It will also

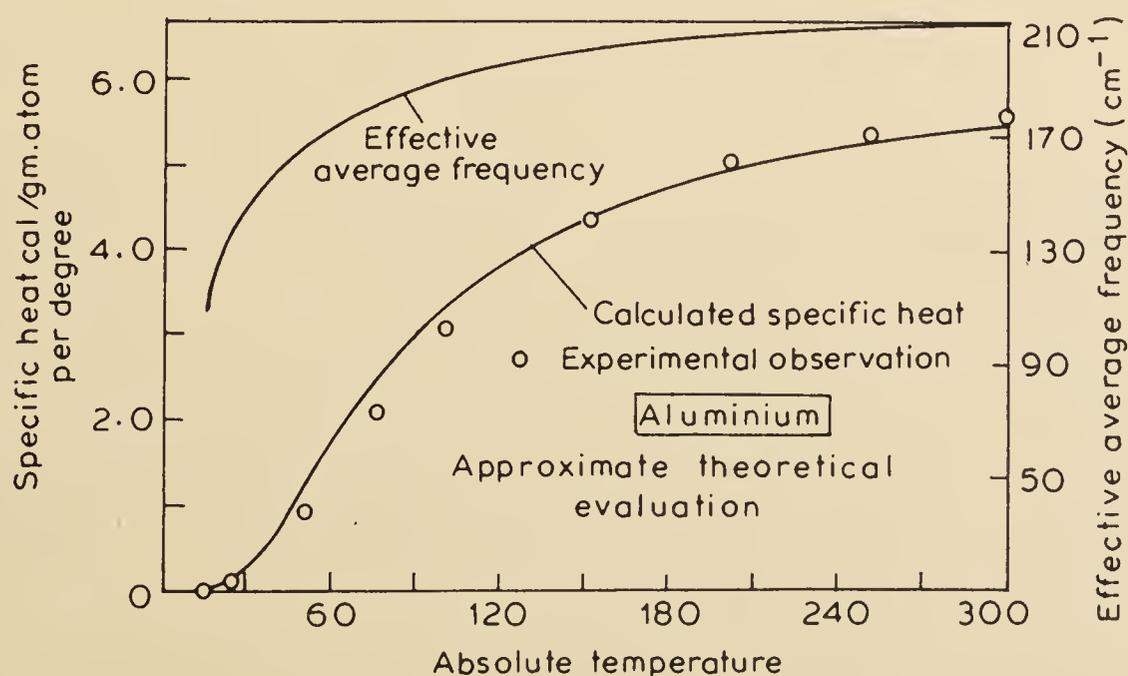


Figure 1. Specific heats of aluminium.

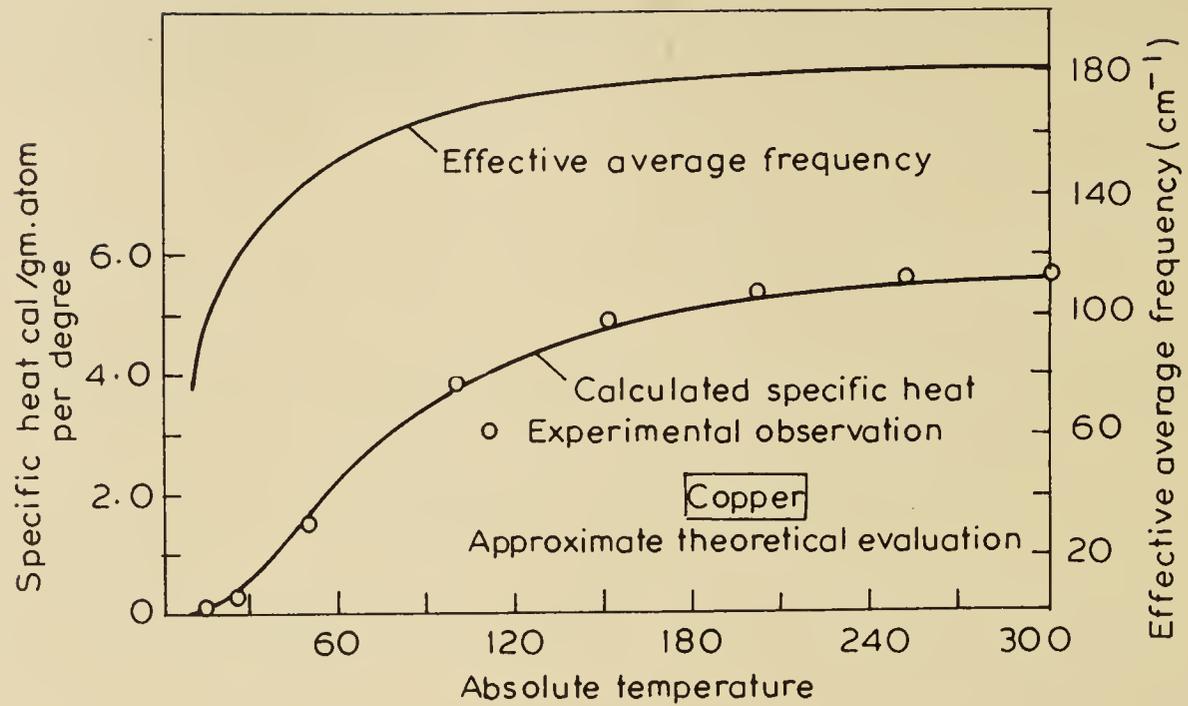


Figure 2. Specific heats of copper.

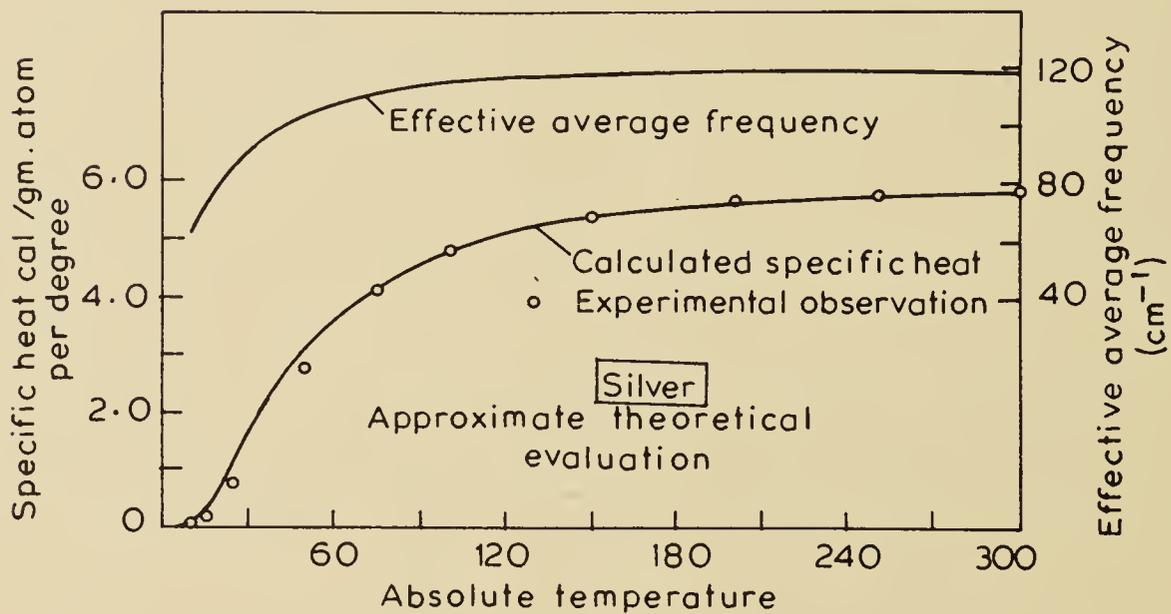


Figure 3. Specific heats of silver.

be noticed that these are equal respectively to the arithmetical average of the four characteristic frequencies of each metal shown at the foot of table 1. The effective average frequency falls off quite slowly as the temperature goes down and hence in the upper part of the temperature range, the arithmetical average frequency determines the course of the specific heat curve. Hence any assumption, however arbitrary, regarding the nature of the atomic vibration spectrum would give the specific heat correctly in this part of the range, provided it gives the same arithmetical average for the atomic vibration frequencies. It is only the steeply falling part of the specific heat curve that is sensitive to the precise nature of the assumed vibration spectrum and can furnish reliable information regarding its true complexion.

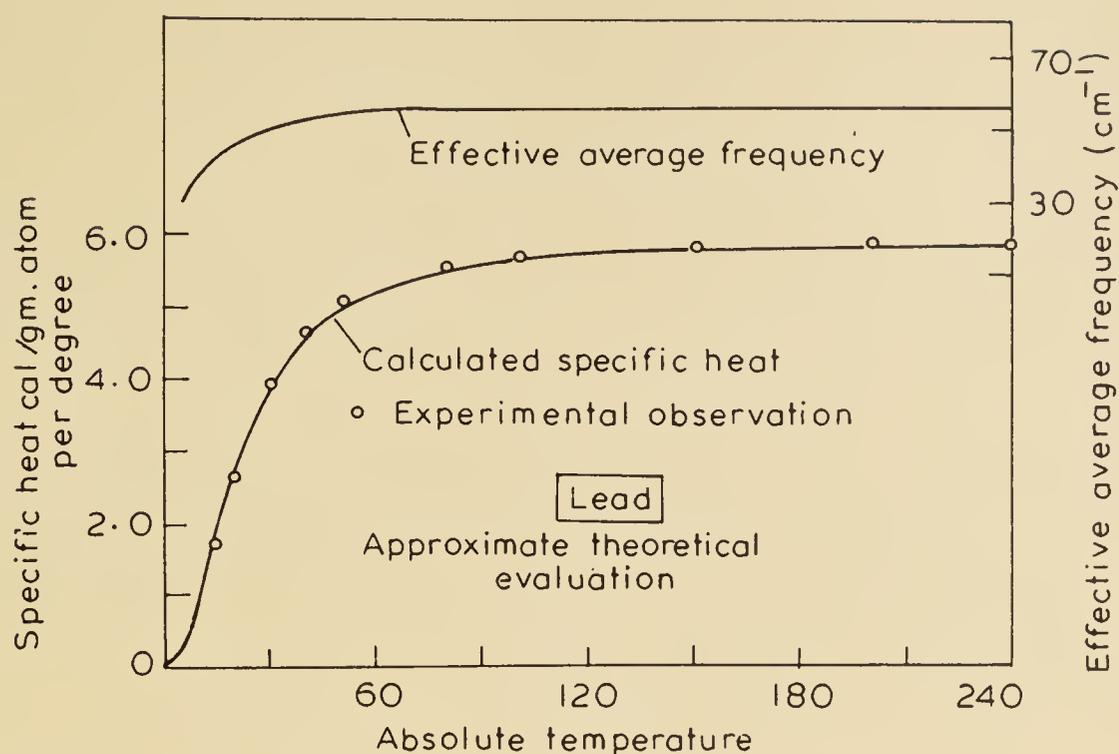


Figure 4. Specific heats of lead.

5. Discussion of the results

In part I of the present series of papers,⁶ an analysis of the results of specific heat determinations by Giaque and his collaborators for these four metals was presented and graphs were reproduced showing the effective average frequency as a function of the temperature. These graphs, unlike those appearing in the present paper, do *not* appear as nearly horizontal lines in the upper part of the temperature range in each case, but exhibit a plateau* in the middle part of the range and then slope down to lower values at the upper limit of the range. It is to be inferred from these consequences deduced from the actual specific heat determinations that the atomic vibration frequencies are themselves not independent of the temperature, and that they (or at least their arithmetical averages) diminish progressively as the temperature rises.

The experimentally determined specific heats^{7,8} have been plotted alongside of the graphs of the calculated specific heats in figures 1, 2, 3 and 4 of the present paper. In view of the remarks made above, it is to be expected that the observed specific heats would lie above the calculated ones in the upper part of the temperature range. It will be noticed from the figures that this is actually the case. The deviations are fairly conspicuous in the case of aluminium and copper, but are less conspicuous in the cases of silver and lead. The characteristic frequencies for aluminium and copper were calculated from the low-temperature elastic constants, while for silver and lead the frequencies were calculated from the

*The plateau frequencies are 206, 167, 113 and 50 cm^{-1} respectively for aluminium, copper, silver and lead. These are somewhat smaller than the arithmetical average frequencies, as is to be expected.

elastic constants at room temperature. The closer approximation actually found between the observed and the calculated specific heats for silver and lead at the higher temperatures is therefore to be expected.

Having regard to the method used for evaluating the four characteristic frequencies, and remembering also that in the present theory we have totally disregarded the anharmonicity of the atomic oscillators, the general agreement between theory and observation over the entire range of temperatures exhibited by figures 1 to 4 may be considered satisfactory. However, it is to be remarked that the observed specific heats are sensibly lower than the calculated ones in the range of temperatures where the specific heat curve slopes steeply down. This is noticeable in the cases of all the four metals and indicates that the characteristic frequencies as determined by the present approximate method need revision. We shall return to this in the third paper of the series.

6. Summary

The specific heats of the four metals aluminium, copper, silver and lead which crystallise as face-centred cubic lattices are evaluated in terms of the four characteristic frequencies of vibration of such a lattice, these latter being determined by an approximate method which relates them to the elastic constants of the crystal. The results thus derived are discussed and compared with the experimentally determined specific heats.

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The specific heats of some metallic elements—Part III. The characteristic frequencies

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1. Introduction

In part I of the present series of papers, the experimental data for the specific heat at constant volume of the four metals aluminium, copper, silver and lead were analysed and discussed. The method of analysis was a determination, with the aid of a table of Einstein's specific heat function, of the frequency of atomic vibration which, if assumed to be common to all the atomic oscillators, would give for the specific heat of the solid its observed value at any given temperature. The frequency thus determined is termed the effective average frequency of the atomic oscillators and is itself a function of the temperature. When this is represented as a graph, it discloses a progressive diminution of the frequency in the upper part of the temperature range covered by the data. Considered in relation to the atomic vibration frequencies themselves, this diminution is least conspicuous in the case of *copper*, while the three other metals aluminium, silver and lead form a sequence in which it exhibits an increasing magnitude.

The explanation of these results is not far to seek. The Einstein formula for the energy of an atomic oscillator as function of its frequency and the expression for the specific heat deduced therefrom by differentiation rest on the assumption that the oscillators are *harmonic*. This assumption is however not strictly justifiable. The expansion of volume which all the metals exhibit with rise of temperature can only be understood if we recognize that the atomic oscillators which are the carriers of the thermal energy are anharmonic in their modes of vibration. Such anharmonicity implies that the vibration frequencies of a quantised oscillator do not form a harmonic sequence but that the successive increments of frequency fall off in a regular progression. Simultaneously also, the dimensions of the oscillator would exhibit a progressive increase which is connected with the magnitude of the vibration and its anharmonicity and hence also with the changes of frequency in a quantitative fashion. It is worthy of remark in this connection that the volume expansion between 0° and 300° absolute in the case of the four metals under consideration is least for *copper*, being 1%, while the three other metals,

aluminium, silver and lead form a sequence in which it progressively increases, being 1.2%, 1.3% and 2.2% respectively for these metals. Thus, there is a clear correlation between the rate of thermal expansion and the rate of change of the atomic vibration frequencies which these metals exhibit at higher temperatures as deduced from their specific heat data.

As is well known, the thermal expansion coefficient of a metal tends to zero at the lowest temperatures and at higher temperatures increases *pari passu* with the specific heat. It follows from these facts and the remarks made above that the specific heats of these metals can be adequately represented by a summation of the Einstein functions for frequencies assumed to be independent of the temperature only over the limited part of the temperature range where the overall expansion of the solid is small and may be ignored without sensible error.

In part II of the present series of papers, the characteristic frequencies for the four metals were evaluated *by an approximate method* based on their relationship to their elastic constants. As was remarked in that paper, the specific heats thus calculated showed distinct deviations from the observed values in the steeply falling part of the curve where its course is specially sensitive to the values chosen for the frequencies. The need for a more precise evaluation was thereby rendered evident. In the present paper, it will be shown that this revision may be effected by making use of the specific heat data themselves in the lower part of the temperature range.

2. The characteristic frequencies

Table 1 below gives the four characteristic frequencies for the four metals calculated approximately from their elastic constants and used in part II. In the adjacent columns are shown the revised values adopted in the present paper. The latter have been determined by trial so as to give the best possible fit with the actual course of the specific heat curve in the lower part of the temperature range in each case. Multiplying each frequency by its degeneracy and dividing the sum total by 21, we obtain the average frequency of the atomic oscillators and this is also shown at the foot of each column.

On an examination of the figures in table 1, it will be seen that in all the four cases, the frequencies as now revised exhibit certain general features in common. Their magnitudes follow each other in the order I, III, II and IV. This is also the order to be expected theoretically, for the cubic spacings are smaller than the octahedral ones and hence should correspond to higher frequencies of vibration, while the longitudinal oscillations in each case should have a notably higher frequency than the transverse ones. Comparing the frequencies determined from the specific heat data with the approximate values estimated from the elastic constants, we also notice certain general features: the frequency of mode I as now deduced is slightly smaller in all the cases; the frequency of mode II is slightly

Table 1. Characteristic frequencies in cm^{-1}

Mode	Degeneracy	Aluminium		Copper		Silver		Lead	
		From elastic constants	From specific heats						
I	3	353	340	260	250	179	179	88	80
II	6	177	200	177	185	109	125	48	45
III	4	287	290	269	215	179	155	87	80
IV	8	145	160	113	120	70	80	30	34
Average		211	222	182	175	117	121	54	53

larger in all the cases except lead; the frequency of mode IV is distinctly larger in all the four cases, while the frequency of mode III is notably diminished in all the cases except aluminium. These alterations have resulted in an increase by a few per cent of the average of the frequencies for aluminium and silver and a diminution by a few per cent of the average in the cases of copper and lead. They have also resulted in bringing the four frequencies for each metal into the proper relationships with each other to be expected in physical grounds, already remarked.

3. The evaluation of the specific heats

Using the values of the characteristic frequencies now adopted, the specific heat for each of the four metals has been calculated by summing up the Einstein functions for the four frequencies and adding the contribution from the continuous spectrum, the upper limit of frequency for the latter being the same as the lowest of the four characteristic frequencies. From the specific heats thus evaluated, the effective average frequencies of the atomic oscillators have also been evaluated as a function of temperature. In figures 1, 2, 3 and 4, these calculations have been represented graphically. The abscissae in the graphs are the absolute temperatures, while the ordinates for the specific heats and for the effective average frequencies appear respectively on the left- and right-hand sides of the figure. It will be seen that the effective average frequency at the upper end of the temperature range is practically the same as the arithmetical average frequency shown at the foot of the columns in table 1 in each case.

The experimentally determined values of the specific heat and the effective average frequencies calculated therefrom have also been shown in the graphs

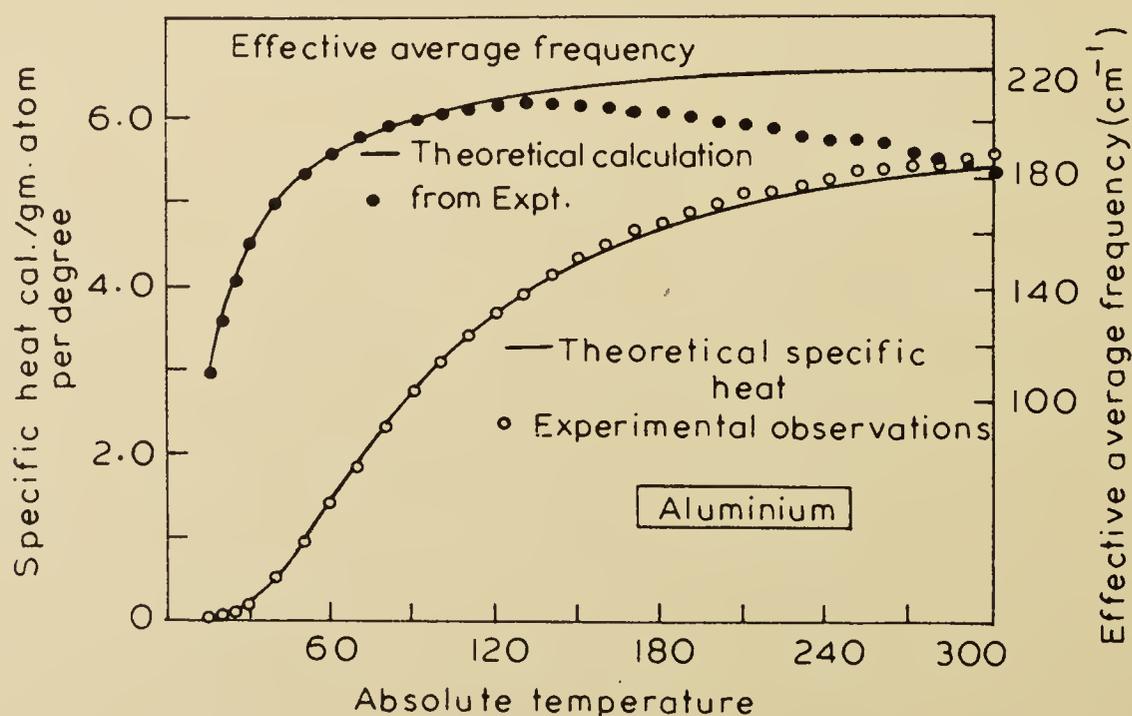


Figure 1. Specific heats of aluminium.

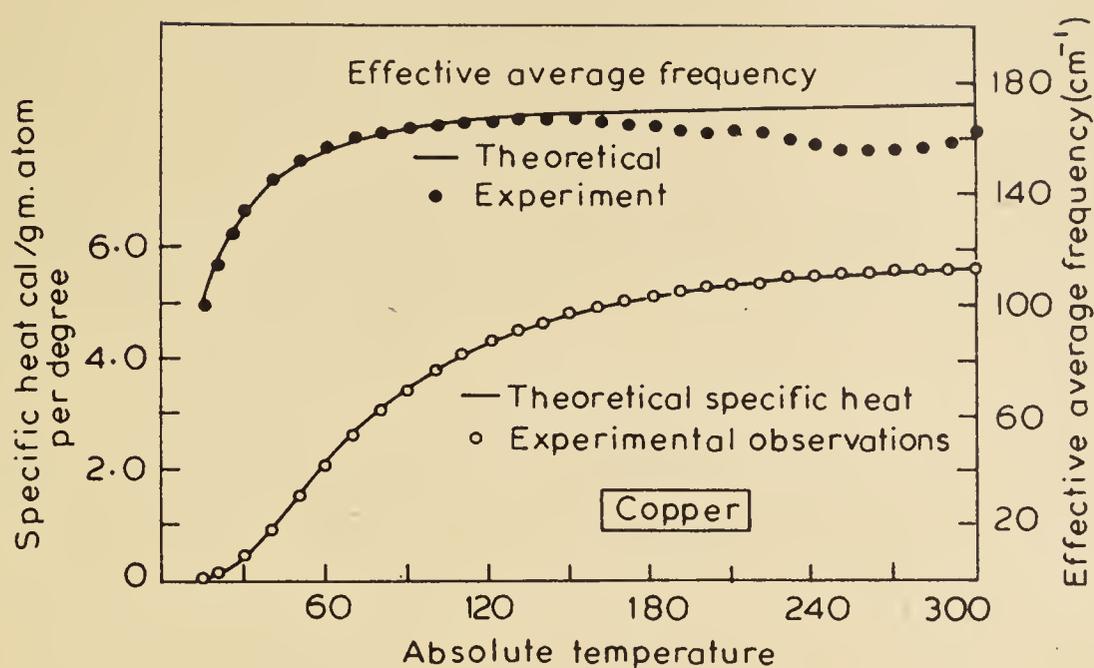


Figure 2. Specific heats of copper.

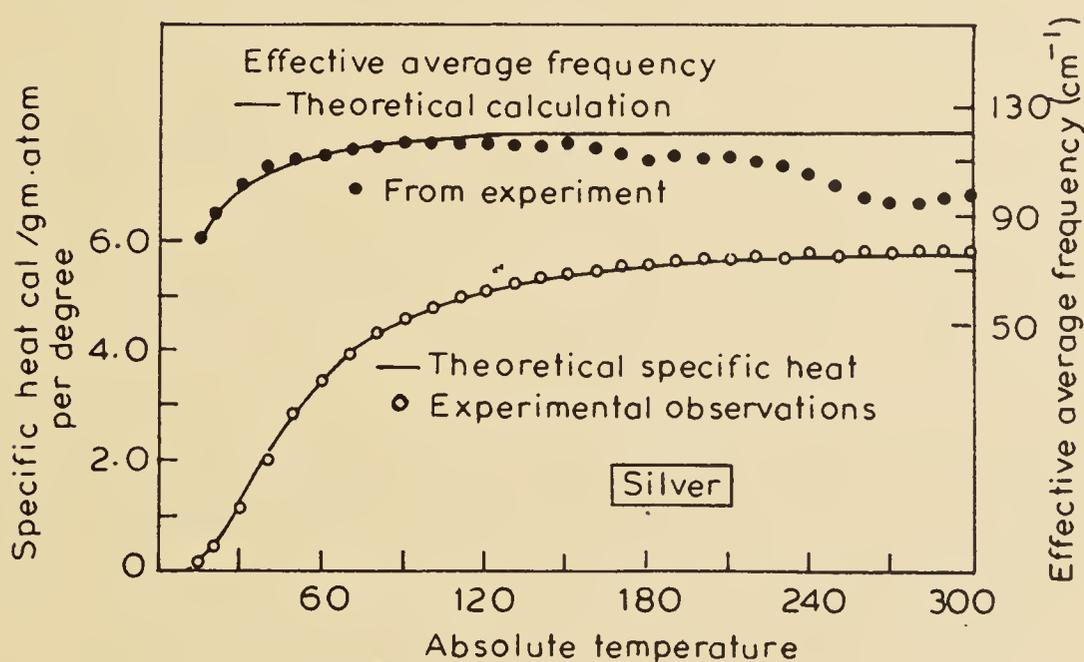


Figure 3. Specific heats of silver.

alongside of the theoretically computed curves in figures 1, 2, 3 and 4. As already stated, the characteristic frequencies employed for the calculation were so chosen as to give the best possible fit with the specific heats in the lower part of the temperature range, i.e., between 15° and 150° absolute in each case. It will be seen that in this part of the temperature range, the observed values fall close to the theoretical curves. On the other hand, in the upper part of the temperature range, i.e., between 150° and 300° absolute, the specific heats observed are consistently higher than the calculated values. The reason for this is evident from the plots of the effective average frequency of atomic vibration. In all the four cases, the atomic vibration frequencies actually effective in the upper part of the temperature range are no longer those deduced from the specific heats at low

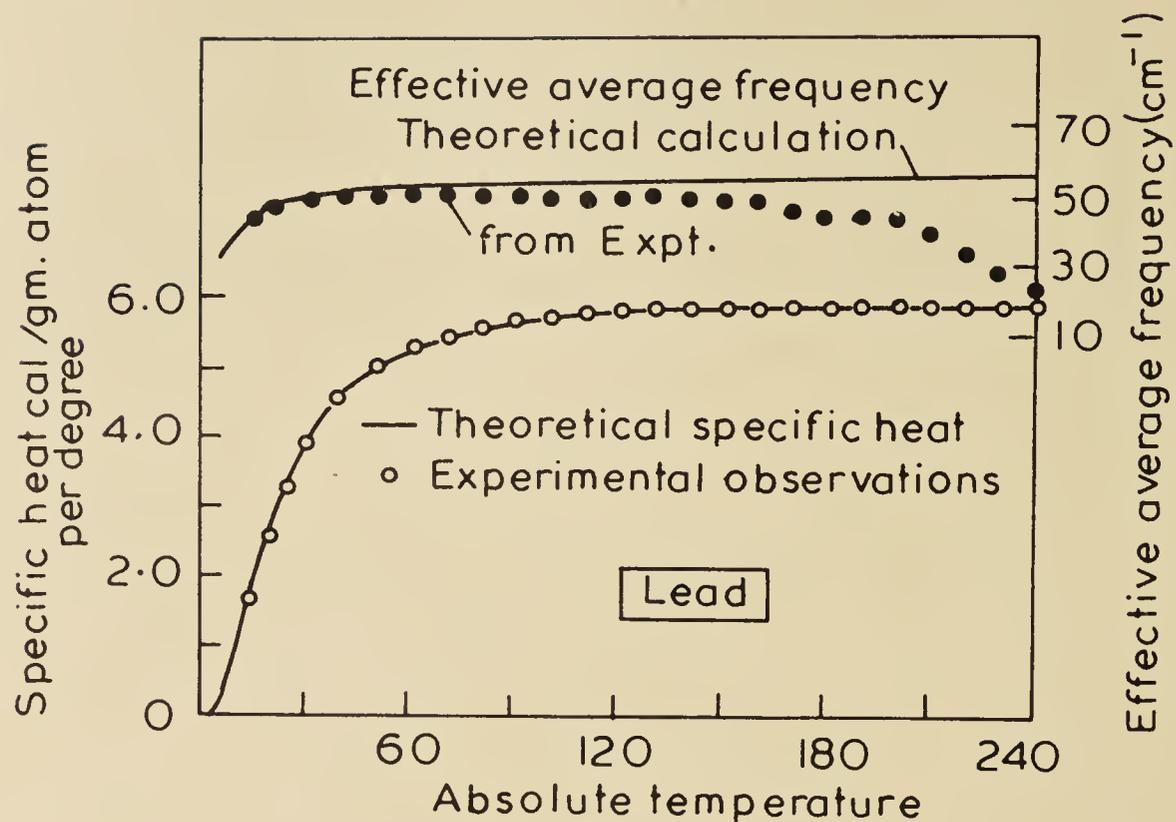


Figure 4. Specific heats of lead.

temperatures but show a progressive diminution with rise of temperature, for the reasons already explained in the Introduction.

Summary

The specific heat data themselves enable us to evaluate more precisely the four characteristic frequencies of each metal determined approximately in part II from their elastic constants. Making use of the new values, the complete specific heat curve is theoretically deduced and shows good agreement with the observations in the lower part of the temperature range, but deviates observably in its upper part, as is to be expected in view of the progressive fall in the frequency of the atomic oscillators with rise of temperature indicated by the analysis of the data in part I. This diminution of the frequencies is a consequence of the anharmonicity of the oscillators which also results in the thermal expansion of the metal. Copper, aluminium, silver and lead form a sequence in the order of increasing coefficients of thermal expansion as also in the magnitude of the temperature coefficients of atomic vibration frequency indicated by their specific heat data.

The specific heats of some metallic elements—Part IV. The residual spectrum

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1. Introduction

The theory of the specific heats of crystals developed in a recent paper by the present author is based on the result that the structure of a crystal containing p atoms in each unit cell has $(24p - 3)$ normal modes of vibration characterised by sharply defined monochromatic frequencies. These may be described as the modes of internal vibration of the groups of $8p$ atoms each included in volume elements of the crystal whose dimensions are twice as large in each direction as those of the unit cell. The three degrees of freedom of atomic movement left out in this description represent the three translations of each group of $8p$ atoms. The vibration spectrum resulting from these translations may be designated as “the residual spectrum” and its nature was discussed in the paper already cited. The contribution to the thermal energy of the crystal arising from the translations of each group of $8p$ atoms is represented by an integral in which Einstein’s expression for the average energy of an oscillator of frequency ν appears multiplied by a quantity $9 \cdot \nu^2 d\nu/\nu_i^3$ and the product is integrated between the limits 0 and ν_i . The upper limit is the upper limit of frequency in the residual spectrum and is also the lowest of the $(24p - 3)$ frequencies characteristic of the structure.

In the case of the metallic elements now under consideration, $p = 1$ and the residual spectrum thus represents only 3 out of every 24 degrees of atomic freedom of movement. It nevertheless plays a major role in determining the magnitude of the specific heat of the metals at very low temperatures. Hence, a comparison of the experimental data at such low temperatures with the calculated values is of importance for establishing the correctness of the present approach to the theory of their specific heats. It is the object of the present paper to present the results of such a comparison.

As the determinations by Giaque and his collaborators which have so far been the basis of our discussion stop at 15°K , we have necessarily to make use of the results reported by other investigators for still lower temperatures. The

circumstance that the specific heats at such temperatures are very low and increase rapidly with rise of temperature sets a limit to the possible accuracy of their experimental determinations. The specific heat also varies enormously from metal to metal and hence even a small percentage of impurity would affect the determined values, raising them or lowering them, as the case may be. These factors may be responsible for the divergences noticed between the results reported by Giaque and collaborators and those obtained by other investigators in the temperature ranges common to them. These divergences are particularly large in the case of aluminium which has a very low specific heat in the range 0 to 15° K but are less serious in the case of the other three metals, copper, silver and lead.

2. The electronic specific heats

The observed variation of the specific heats of metals with temperature in the vicinity of the absolute zero differs in its features from that observed in the case of insulators, e.g., diamond or the alkali halides. The curves do not touch the axis of the abscissae but meet it at the origin making a definite angle with it. The specific heats in this region can be represented by an expression of the form $AT + BT^3$. These facts are explained on the basis that the first term represents the contribution arising from the thermal agitation of the electrons and the second from the thermal agitation of the atoms themselves. This interpretation finds support in the fact that in the case of metals exhibiting superconductivity, e.g., aluminium and lead, the coefficient A exhibits a distinctly larger value in the range of superconductivity, while the coefficient B remains unaltered.

Table 1. Specific heats at low temperatures
 $C_v = AT + BT^3$

Substance	Range of measurement	$A \times 10^4$	$B \times 10^5$	Auhtor
Aluminium	0–20° K	3.48	0.63	Kok & Keesom
	0– 4° K	3.42	0.68	Howling <i>et al</i>
Copper	0–20° K	1.78	1.24	Kok & Keesom
	0– 5° K	1.64	1.14	Corak <i>et al</i>
Silver	0– 5° K	1.46	4.06	Corak <i>et al</i>
Lead	0– 5° K	7.48	52.04	Horowitz <i>et al</i>

Table 1 shows the results for the four metals now under consideration reported by various authors. It will be seen that the coefficient A is largest for lead; aluminium stands next and is followed by copper and silver, the coefficients for

the latter not being very different. The value quoted in the case of lead is for the state of the metal in which the superconductivity has been eliminated by a strong magnetic field.

It follows from what has been stated above that for a comparison of the experimental data with the results of the present theory, it is necessary to add to the specific heat a term representing the electronic contribution. This has been done, making use of the results of the authors quoted in the table. We shall discuss first the results thus obtained in the case of copper, silver and lead, since in the cases of these metals the determinations which we make use of are in reasonable agreement with those reported by Giaque and collaborators. The case of aluminium where this is not the case will also be discussed.

3. Comparison of theory and experiment

Copper—The specific heat of copper in the range between 0° and 20° K has been reported by Kok and Keesom, while in the more limited range from 0 to 5° K measurements have been made by Corak, Garfunkel, Satterthwaite and Wexler.

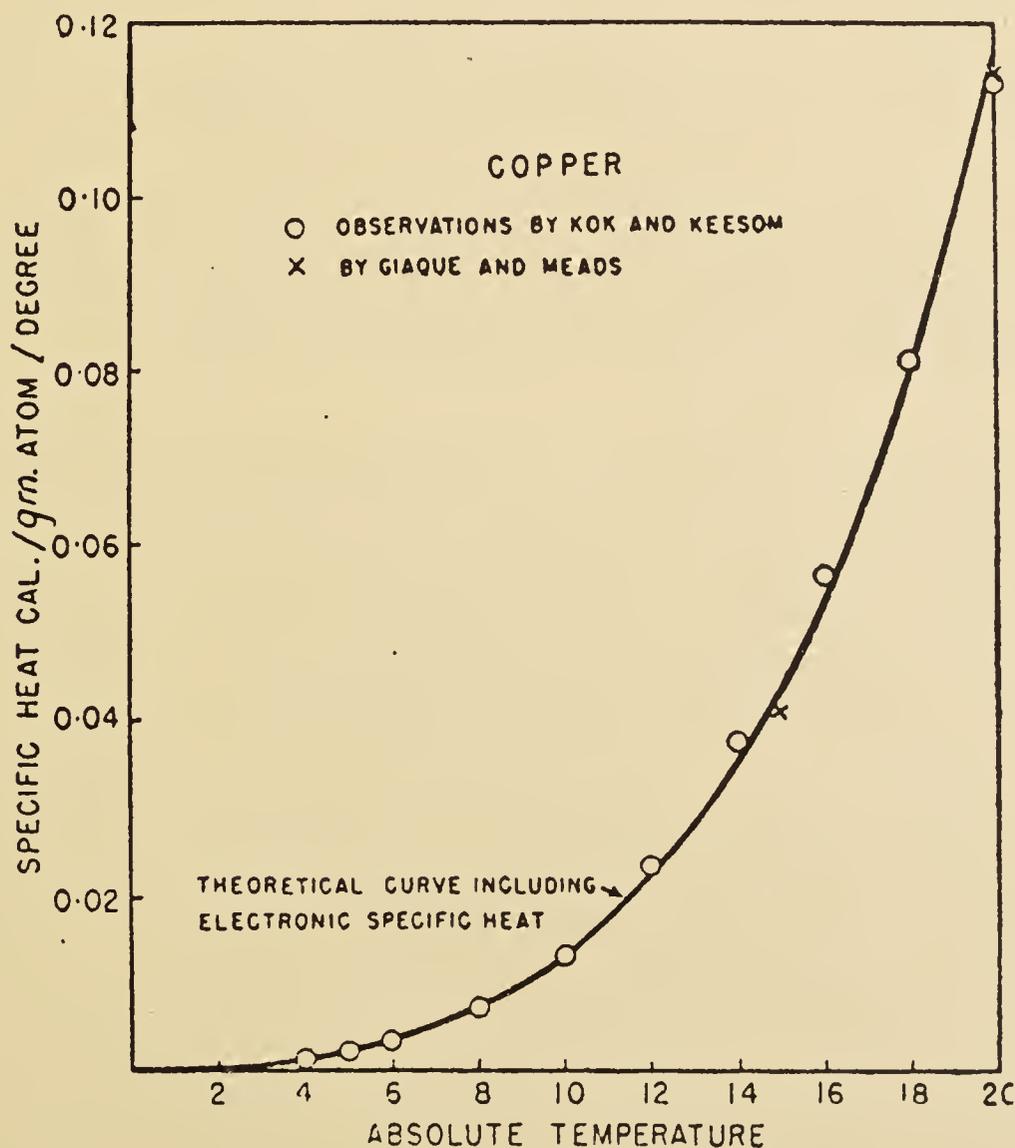


Figure 1. Specific heats of copper.

We present the comparison between theory and experiment in the form of two graphs, one in the range 0 to 20° K and the other in the range 0 to 5° K. In the latter range the results of Kok and Keesom are systematically in excess of those reported by Corak *et al*, the difference being about 8% at 5° K. However, a satisfactory overall agreement between theory and experiment is exhibited by both the graphs.

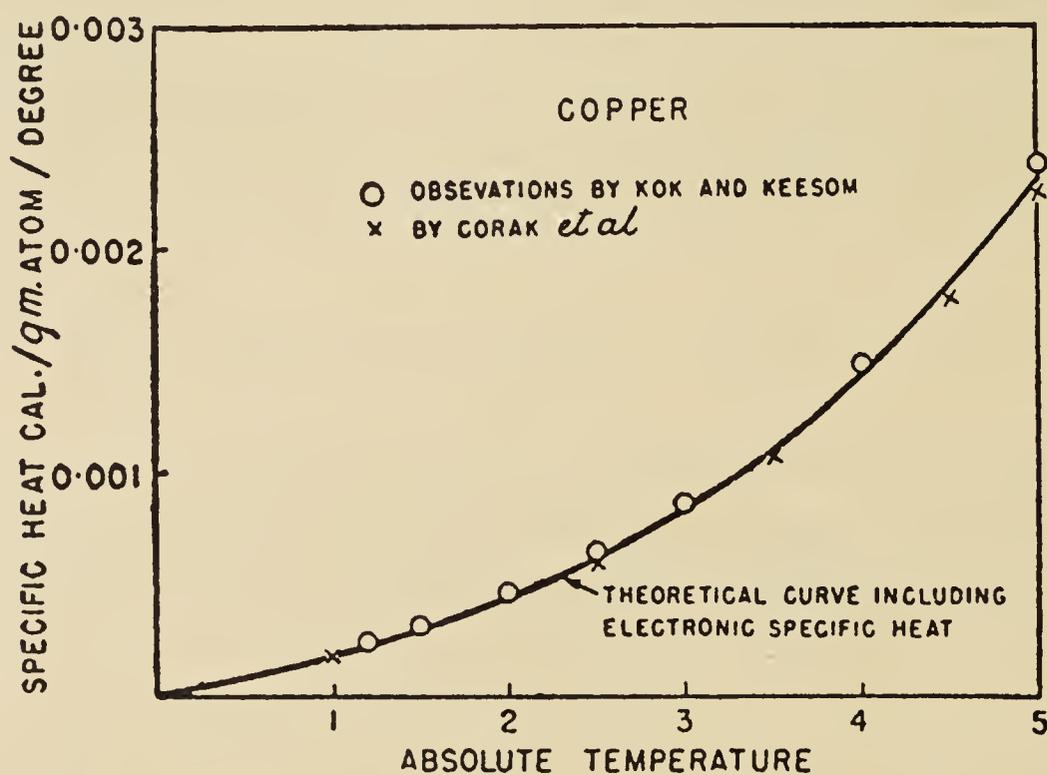


Figure 2. Specific heats of copper.

Silver—Likewise in the case of silver we present the results in the form of two graphs, figures 3 and 4 respectively. Here again, a satisfactory agreement emerges between the theoretical results and the experimental data.

Lead—All the four characteristic frequencies besides the residual spectrum contribute to the observed specific heat at 20° K and this continues to be the case upto 10° K. At still lower temperatures the contributions of only the lowest of the four characteristic frequencies and the residual spectrum predominate. Below 5° K, only the residual spectrum is of importance. As in the previous cases we present a comparison between theory and experiment in the form of two graphs covering the ranges 0 to 20° K and 0 to 5° K as figures 5 and 6 respectively. In figure 5 the available determinations of various authors have all been plotted and it will be seen that between 15° and 20° K the determinations agree generally with each other and with the course of the theoretical curve. Between 5° and 15° K the only observations are those by Keesom and Van den Ende whose results appear to be rather erratic but nevertheless follow the trend of the theoretical curve fairly well. At the lowest temperatures the results of these same authors are noticeably in excess of those deduced from theory. But as will be seen from figure 6 the observations by Horowitz *et al* are in excellent accord with the calculated values.

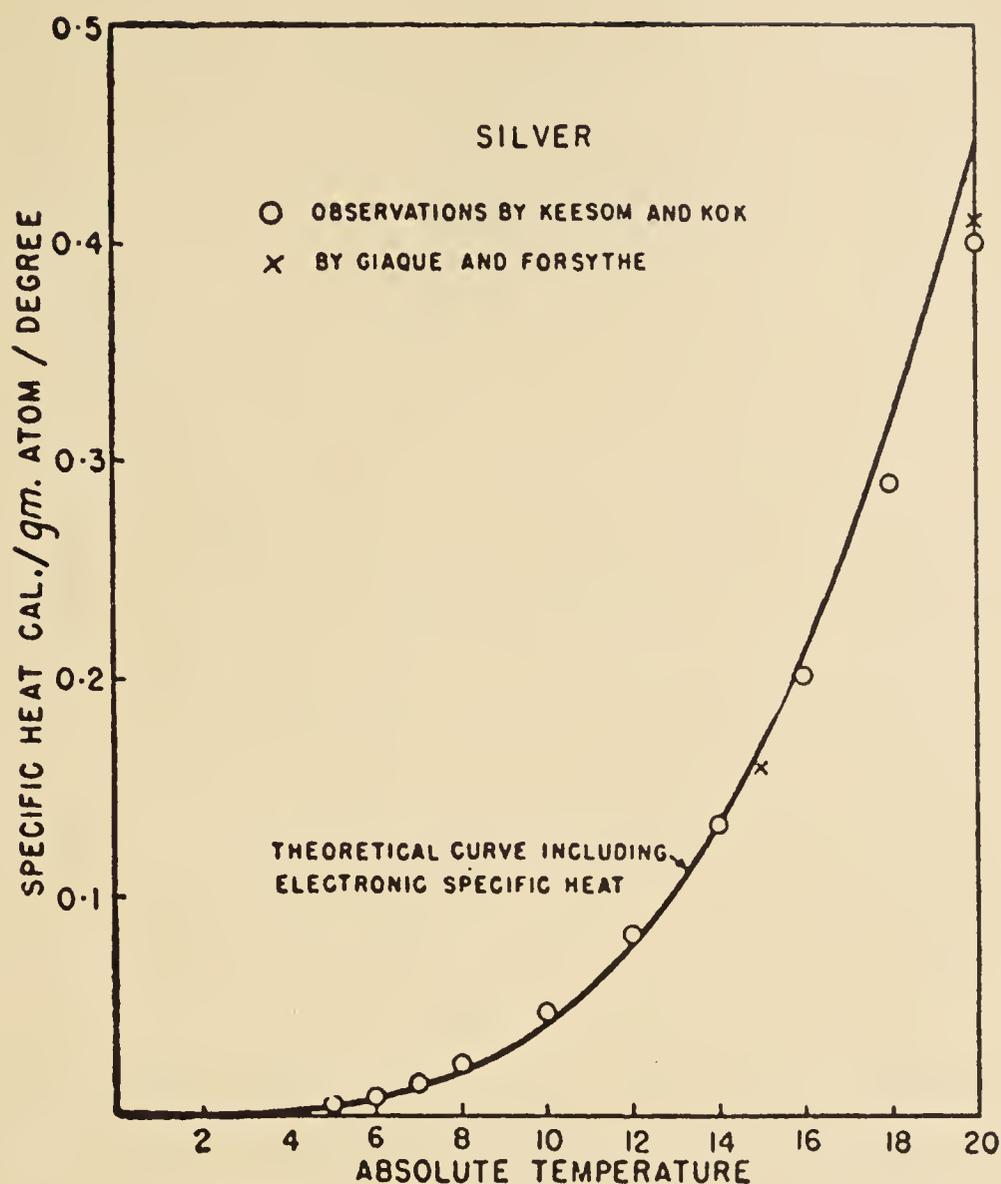


Figure 3. Specific heats of silver.

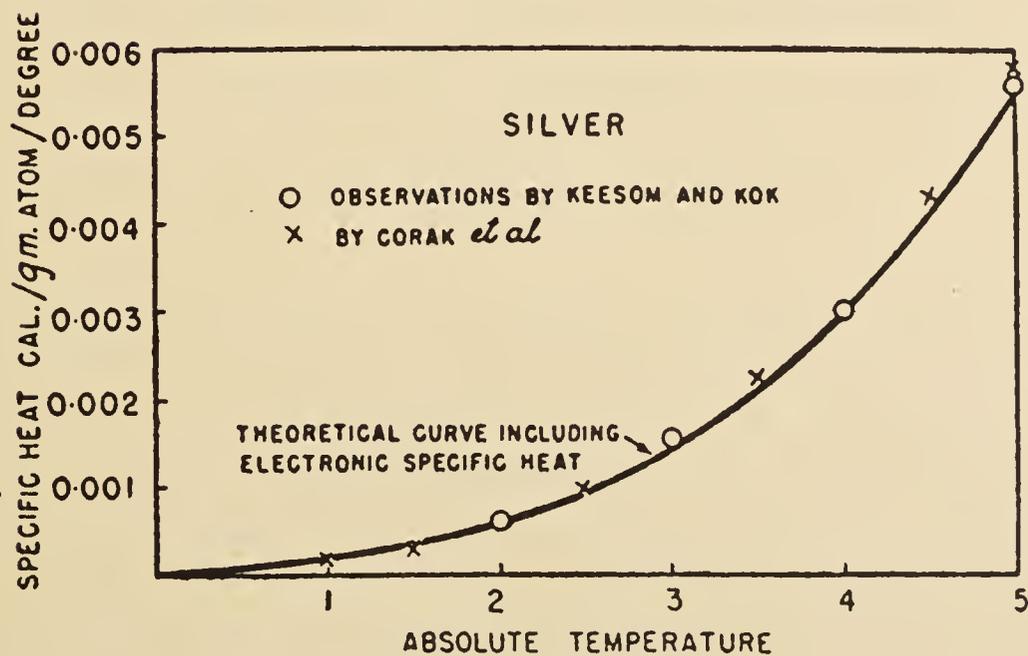


Figure 4. Specific heats of silver.

Aluminium—Of the four metals studied, aluminium has the lowest specific heats in the range 0 to 20° K, and the electronic contribution forms an important part of the whole. Making use of the characteristic frequencies deduced in part III from

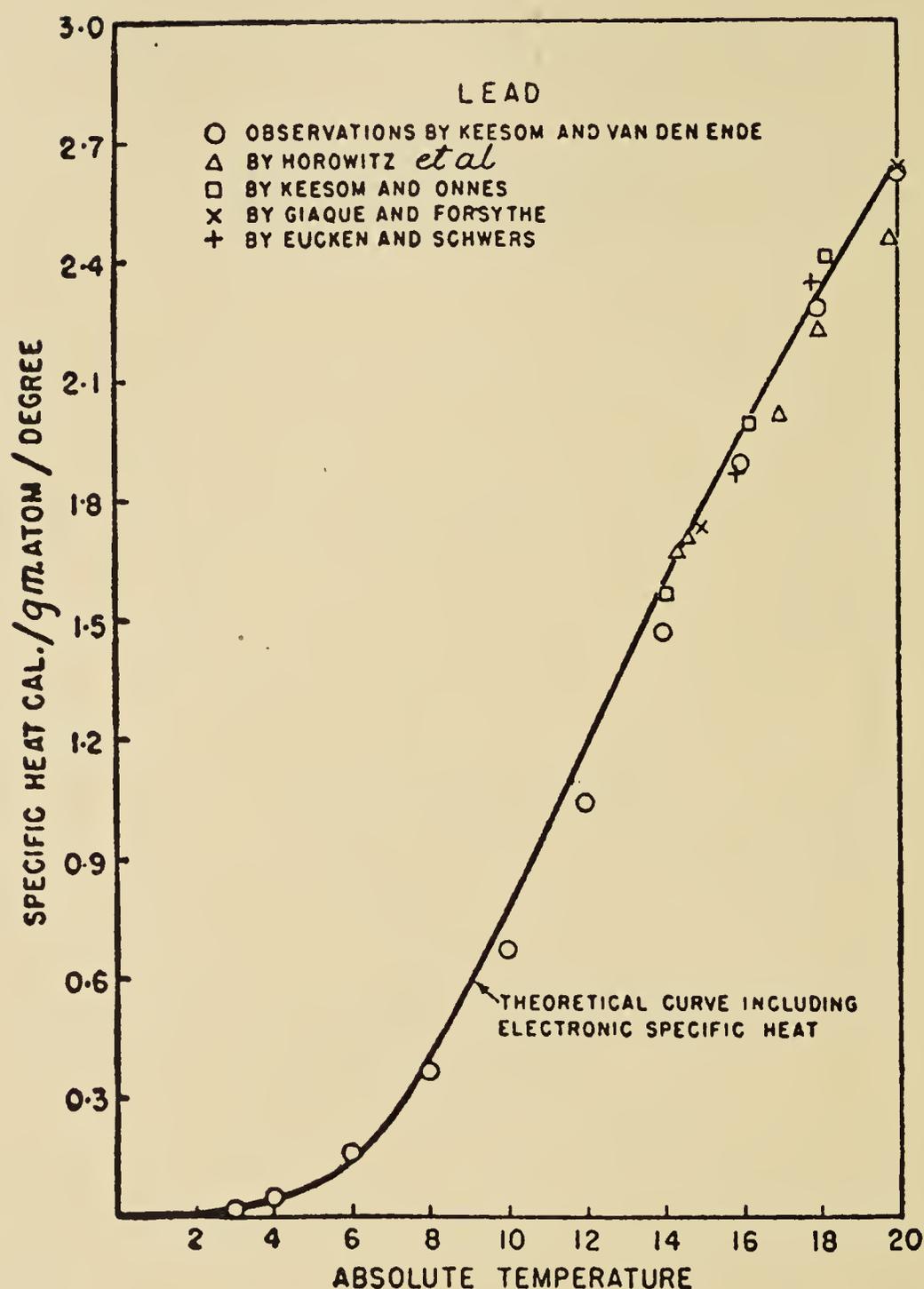


Figure 5. Specific heats of lead.

the specific heat data themselves as reported by Giaque and Meads and taking into account the electronic contribution, the specific heat curve has been computed. The graph thus obtained coincides with the observations reported by Kok and Keesom only at the lowest temperatures where the electronic heat contribution predominates. In the range from 5 to 20° K, the data reported by Kok and Keesom deviate progressively from the theoretical curve, the observed values being everywhere in excess by quantities ranging from 8 to 20% of the calculated ones. They are also in excess of the values reported by Giaque and Meads for 15° and 20° K to a similar extent.

Throughout the range now under discussion the specific heat of aluminium is determined solely by the contribution of the residual spectrum with the addition of the electronic specific heat. The values reported by Kok and Keesom throughout the range would be in fair agreement with the theoretical calculations

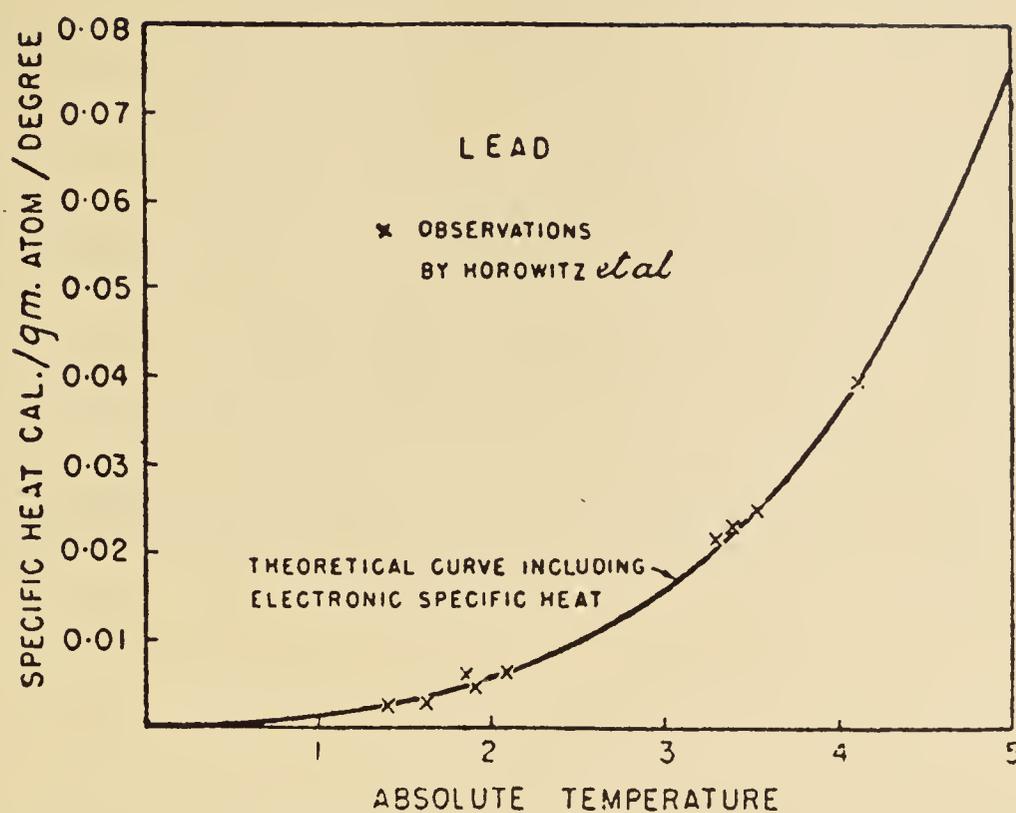


Figure 6. Specific heats of lead.

if the upper limit of frequency in the residual spectrum were taken as 146 cm^{-1} which is nearly the value deduced in part II by an approximate method instead of as 160 cm^{-1} calculated in part III from the specific heat data themselves. But the former assumption would result in the theoretically calculated values at higher temperatures differing from those reported by Giaque and Meads by more than the probable magnitude of their experimental errors. Considering these facts, it appears correct to assume that the values reported by Kok and Keesom for aluminium in the upper part of the temperature range between 0 to 20° K are in excess of the real values by quantities of the order of 10%.

Summary

The theoretical calculation of the specific heats of the four metals aluminium, copper, silver and lead which in part III were shown to be in satisfactory accord with the experimental data reported by Giaque and collaborators in the range from 15 to 300° K have in the present paper been extended down to the absolute zero. When the contribution arising from the thermal agitation from the electrons is included, the calculated specific heats are in satisfactory accord with the results reported by various investigators on the low temperature specific heats of these metals. The agreement is excellent in the cases of copper, silver and lead, but not so satisfactory for aluminium, the available data for which are meagre and appear to be of doubtful accuracy.

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The specific heats of crystals and the fallacy of the theories of Debye and Born

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1. Introduction

The first step in any attempt at a theoretical evaluation of the specific heats of crystals is to determine the nature of the disturbance in their structure produced by the thermal agitation. In an earlier publication¹ and more fully again in the address to the Conference of Nobel Laureates held at Lindau in June 1956 which was printed in these *Proceedings*,² this problem was discussed. A general theory of the specific heats of crystals embodying the ideas expressed in those memoirs has since been formulated and published.³ The theory leads to a determination of the spectroscopic behaviour of crystals and simultaneously with it to an expression for their specific heats as a function of the temperature. The success of the theory in achieving these aims has been demonstrated by a series of fully worked-out examples and a comparison with the facts of experiment.⁴

The principles on which the present approach to specific heat theory is based may be briefly sketched here. While the classical mechanics is made use of in the theory, stress is laid on the necessity of paying due regard at the same time to the basic principles of thermodynamics and to the fundamental notions of the quantum theory. With these requirements in view, the crystal is regarded as an assembly in thermodynamic equilibrium of sets of *similar* oscillators in great number, the energies of vibration of which are *individually* quantised. The identification and enumeration of these oscillators and the determination of their modes and frequencies of vibration is accomplished by taking note of the three-dimensional periodicity of structure characteristic of crystals and applying to the elements of that structure essentially the same methods as those which are so successful in the field of molecular spectroscopy. The determination of the thermal energy of the crystal as a function of the temperature is then effected by the same procedure as that indicated by Einstein in his fundamental paper⁵ of 1907 introducing the quantum theory of specific heats.

The present approach to specific heat theory rejects completely the ideas regarding the subject embodied in Debye's well known paper⁶ and also those set

out by Born and his school in numerous publications.⁷ As the present generation of physicists and chemists has been brought up to believe in these latter theories, it would not be superfluous to explain in some detail why their rejection is necessary. That indeed is the purpose of the present memoir, which is sought to be achieved by a searching examination of the premises underlying the theories of Debye and Born and of the consequences to which those theories lead. It emerges from the examination that those premises are untenable and that the conclusions derived from them are false.

2. The hypothesis of Jeans

The parent of the specific heat theories of Debye and Born and also of other similar theories was a publication⁸ by J H Jeans which appeared in the *Philosophical Magazine* in the year 1909. Though the title of that paper indicated temperature radiation as its subject, actually it was devoted for the most part to a discussion of the thermal behaviour of material bodies on the basis of classical mechanics. It put forward and sought to establish a proposition which may be stated as follows: *the thermal energy of material bodies is identifiable with the sum of the potential and kinetic energies of regular trains of waves traversing them and forming stationary wave-patterns filling their volume.* The reader familiar with Debye's specific heat theory will immediately recognise this as the thesis which Debye accepted and elaborated in his attempt to explain the experimental results for the specific heats of elementary solids at low temperatures. It is not surprising in these circumstances that Jeans became an enthusiastic supporter of Debye's theory and by his advocacy helped to promote a general belief in the validity of the thesis on which that theory was based.

The waves considered by Debye in his paper were the longitudinal and transversal waves in an isotropic solid contemplated by the classical theory of elasticity. The formulae set out in the paper were based on an analysis of the modes of vibration of an elastic solid sphere whose external surface was assumed to be rigidly fixed, followed by their enumeration in terms of their frequencies of vibration. Debye restricted himself for the most part to a consideration of the cases of monatomic solids exhibiting cubic symmetry. No such restriction is contemplated in the theory put forward and developed by Born and his school, which claims to be valid for all crystals. While Debye considered it to be adequate for his purpose to regard the vibrating solid as a continuum, the Born theory claims to take account of the discrete lattice structure of the crystal. The waves considered in it are also of more general kind than those recognised by Debye. Nevertheless, the theory of Born, like that of Debye, is based on an acceptance of the same thesis, viz., the hypothesis of Jeans.

3. The fallacy of the hypothesis

Simple considerations of a general character suffice to show that the hypothesis of Jeans is a wholly misconceived idea. We have only to remark that the specific heat of a solid is an atomistic property, since its value at any given temperature is completely determined by two quantities, one of which is the number of atoms comprised in unit mass of the substance, and the other is the effective average frequency of vibration of the atoms at that temperature. Any attempt to explain this situation theoretically has, of necessity, to base itself on an atomistic approach to the problem. In other words, we have to consider the individual atoms in the crystal and investigate their dynamic behaviour. *Per contra*, wave-motions and the stationary wave-patterns resulting from the presence of an external boundary limiting their travel are macroscopic concepts, which, it should be emphasised, do not require us to take any notice of the atomicity of structure of the material traversed by the waves. In these circumstances, it is obvious that the attempt to build a theory of specific heats on the assumption that the thermal agitation is identifiable with wave-motions is an illogical and illusory proceeding.

We may usefully enlarge upon the foregoing remarks. The specific heat theories based on the hypothesis of Jeans concern themselves with the enumeration of the stationary wave-patterns assumed to exist within the volume of the solid. But, since the atomicity of structure of the material need not at all be considered in the description and enumeration of the wave-patterns, it remains completely outside the problem. The identification of the thermal energy of the solids with the sum of the kinetic and potential energies of the wave-patterns is therefore incapable of leading us to any determination of their specific heats. The difficulty which arises here is one of pure logic and is fundamental. In the theories now under discussion, the difficulty is sought to be circumvented by introducing an additional assumption, viz., that the total number of wave-patterns is equal to thrice the number of atoms comprised in the crystal. While this assumption may appear plausible, it cannot be pretended that such a fixation of the number of wave-patterns is a necessary consequence or concomitant of the wave hypothesis. Actually, of course, it is introduced in order "to make the theory work", in other words, in order that the results of the theory might bear some resemblance to the experimental facts. In logic, such a proceeding would be described as *petitio principii*, or begging the question.

4. Thermodynamics and the theory of specific heats

It can be readily shown that the notions underlying the theories of Debye and Born are irreconcilable with the statistical concept of the nature of thermal energy which lies at the very base of the science of thermodynamics. A crystal is an

assembly of an immense number of individual atoms which are capable of moving from their positions of equilibrium. Hence, the state of the system can only be described in terms of the values of a very large number of independent variables. No doubt, the atoms are held together by their mutual interactions to form the ordered assemblage which we call a crystal and which can be regarded as a unit in the macroscopic sense. But the statistical concept of thermal energy forbids us from regarding the entire assembly as a single unit in the thermodynamic sense. We cannot, for example, identify the thermal energy of the crystal with the energy of stationary wave-patterns of any sort. Indeed, the constancy of amplitude and coherence of phase relationship over extended regions of space and large periods of time which the formation of such wave-patterns presupposes are excluded by reason of the very nature of thermal energy. *Per contra*, it is to be expected that the thermal energy of a solid exhibits fluctuations in space and in time which preclude any definitive description of it except for domains of space and periods of time which are very small in comparison with macroscopic standards.

5. Classical mechanics and the theory of specific heats

That the theories of Debye and Born are untenable become evident also when we examine them from the standpoint of classical mechanics. For, specific heat theory starts from the well known theorem that all the possible vibrations of a system of connected particles are superpositions of a set of normal modes in each of which the particles oscillate with the same frequency and in the same or opposite phases. The particles in the present problem are the individual atoms in the crystal and hence we are here concerned with the determination of the normal modes of vibration of *the atoms* in the sense of the theorem just stated. Instead of considering this question, the theories of Debye and Born concern themselves with an entirely different and indeed irrelevant subject, viz., the normal modes of vibration of a macroscopic solid as determined by the form of its external boundary. Their treatment of specific heat theory thus stands revealed as a purely fanciful approach devoid of any validity or significance.

A straightforward application of the standard methods of classical dynamics enables us to determine the characteristic modes and frequencies with which the atoms in a three-dimensionally periodic array can oscillate about their positions of equilibrium. It emerges from the investigation that these characteristic modes can be enumerated and that they are related in a precisely definable manner to the structure and symmetry properties of the atomic groupings in the crystal. In the theories of Debye and Born, on the other hand, which assume that the modes of vibration are determined by the external boundary conditions and further, that the total number of wave-patterns is equal to thrice the number of atoms included in the crystal, we encounter results of an altogether different character. According

to these theories, the great majority of the stationary wave-patterns which they contemplate have "wavelengths" of the same order of magnitude as the lattice-spacings of the crystal. But these wavelengths are all different and represent different frequencies of vibration. As a consequence, the "cells" of the wave-pattern in which the phase of vibration alternates bear no relation whatever to the structure of the crystal, while the wave-patterns themselves appear in immense numbers and are all different from each other. Such a description of the dynamical behaviour of the atoms linked with one another in the geometrically ordered structure of a crystal is, on the face of it, a fantastic misrepresentation. It is, in effect, a *reductio ad absurdum* of the theories which lead up to it.

6. The quantum theory of specific heats

The ideas which connect the hypothesis of energy quanta with the theory of specific heats were very clearly expounded in Einstein's classic paper⁵ of 1907. If it be assumed that radiation is emitted or absorbed in energy-quanta proportional to the frequency, it follows as a necessary consequence that the mechanical energy of the oscillator which thus emits or absorbs would itself diminish or increase respectively by finite steps of the same amount. Generalising this result, Einstein postulated that the energy of any elementary structure capable of mechanical vibration would likewise obey the quantum rule. He then coupled this with the concept of thermodynamic probability embodied in Boltzmann's principle and showed that the relative probabilities of the oscillator being in different energy states could be determined with the aid of the principle. The next step is the evaluation of the average energy of an oscillator in an assembly consisting of a great number of such oscillators having a common frequency of vibration. This leads at once to the evaluation of the thermal energy of the whole assembly. The basic ideas of the quantum theory were further clarified and illumined by Einstein in the famous paper⁹ of 1917 in which he showed that the exchange of energy between a radiation field and the oscillators located in it can properly be described only in terms of statistical concepts. The probability of the oscillator being in any given state appears in the paper as the product of two factors, one of which is the thermodynamic probability factor given by the Boltzmann formula and the other is the intrinsic statistical weight of that state.

The foregoing remarks are made to emphasise that the quantum theory of specific heats rests on thermodynamic-statistical concepts which are wholly alien to the determinism of macroscopic physics. In other words, the theory of energy-quanta possesses a meaning and significance only in relation to the behaviour of the ultimate units of which matter is composed; *per contra* it is wholly out of place in any considerations regarding the behaviour of matter in bulk. For example, we can speak of the energy states of rotation or vibration of a molecule of benzene,

but it would be nonsensical to discuss the problem of quantising the vibration of a tuning fork or the rotations of a fly-wheel.

It will be clear from the foregoing remarks that Debye and Born fell grievously into error when they rejected the basic ideas of Einstein's theory and sought to build a theory of the specific heats of crystals on the behaviour of macroscopic solids. In doing this, not only did they ignore all considerations of logic as well as the physical principles bearing on the subject, but they also sought to impose on the quantum theory a fantastic and altogether meaningless interpretation.

7. The spectroscopic behaviour of crystals

The specific heats of crystals and their spectroscopic behaviour are intimately related properties since they are both determined by the frequencies of vibration of the atoms about their positions of equilibrium. This relationship is conveyed more precisely by the statement that the elementary oscillators in the crystal which are the carriers of its heat energy are also the oscillators capable of absorbing, emitting or scattering the radiations incident on it. It follows that any valid specific heat theory contains within itself a complete description of the vibration spectrum of a crystal: vice versa, a theory of the spectroscopic behaviour of crystals which correctly describes the facts of observation in that field necessarily contains within itself all the data needed for the evaluation of the specific heat as a function of the temperature.

From the foregoing remarks, it follows that the theories of Debye and Born which are based on erroneous assumptions regarding the carriers of the thermal energy in crystals also lead to a false picture of their vibration spectra. That is actually the case, for the assumptions made in these theories lead to the conclusion that the vibration frequencies of a crystal are immensely numerous and are all different from each other and hence that the vibration spectrum exhibits a continuous band of frequencies stretching over the entire range. *Per contra*, the atomistic theory of specific heats shows that the vibration spectrum of a crystal consists of a finite number of discrete monochromatic frequencies accompanied by a residual spectrum with a relatively small statistical weight which may be considered as continuous and which goes down to very low frequencies.

Spectroscopy is an exact science, and the vibration spectra of crystals are accessible to precise study and investigation by several different techniques and with a great variety of materials. In every case, the experimental results support and confirm the results of the atomistic theory in an unequivocal fashion. They are therefore also an objective demonstration of the falsity of the Debye and Born theories.

8. Summary

It is shown that the hypothesis, originally proposed by Jeans and adopted in the theories of Debye and Born, that the thermal energy of a solid is identifiable with the energy of wave-motions in its interior is not logically sustainable as a basis for a theory of their specific heats. The constancy of amplitude and of phase-relationships in extended volumes and periods of time demanded by the hypothesis is irreconcilable with the statistical-thermodynamical concept of the nature of thermal energy, and the idea that the theory of specific heats can be treated as a boundary-value problem in the physics of macroscopic solids is therefore misconceived. It is shown that such an approach is repugnant both to classical mechanics and to the principles of the quantum theory. It must therefore give place to a purely atomistic approach which gives us a wholly different picture of the nature of the thermal agitation in the solid and of its vibration spectrum.

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The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part I. The results of experimental study

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1. Introduction

The fundamental questions requiring an answer which arise in relation to the infra-red behaviour of crystals are the following: What is the nature of the vibration spectrum of the atomic nuclei in a crystal? How is this vibration spectrum related to its observed infra-red absorption spectra? What is the mechanism of the reflection and of the absorption of infra-red radiation by crystals? A precise and detailed experimental study of the infra-red behaviour of some crystals of simple structure may be expected to furnish an answer to these questions.

Magnesium oxide crystallises in the cubic system and, if the material is pure, the crystals are transparent and colourless. The structure of MgO is similar to that of rock-salt and is thus very simple. Moreover, the binding forces between the atoms being much stronger and their reduced mass much smaller for MgO than for NaCl, the infra-red absorption of MgO appears in a region much more readily accessible to precise investigation than that of rock-salt. Hence, MgO would be a most appropriate choice of material for a study of the kind referred to above.

A collection of MgO crystals came into the writer's hands many years ago as a gift from the Norton Company of Worcester, Mass., USA. Somewhat later, a single crystal of large size was received by him from AD Mackay, Inc. of Broadway, New York. It had long been the intention of the writer to make use of this material for a thorough investigation of the kind envisaged in the foregoing paragraphs. Only recently, however, has the availability at this Institute of an infra-red recording spectrograph by Messrs Leitz of Wetzlar provided with both NaCl and KBr optics enabled this desire to be fulfilled. The results of the experimental study made with this instrument are described and discussed in this first part of the memoir. In the subsequent parts of the memoir, their theoretical implications and their further consequences are worked out.

The reflecting power of a freshly cleaved surface of an MgO crystal relative to an aluminium mirror was determined by Burstein, Oberly and Plyler (1948) for the spectral region between $10\ \mu$ and $35\ \mu$ and the results were presented in a paper published in these *Proceedings* some years ago (*Proc. Indian Acad. Sci.*, 1948, A28, 388). The same authors also recorded the transmission of infra-red radiation in the wavelength range between $5\ \mu$ and $13\ \mu$ of five cleavage plates of MgO of thicknesses ranging from 9.2 to 0.9 mm. Graphs showing these five transmission curves (in part) and grouped together were reproduced as a figure in the same paper. As regards the reflecting power of MgO, the work of Burstein, Oberly and Plyler was complete and their results will be made use of and discussed in the present memoir. The position is rather different with reference to their studies of the transmission through MgO. Their work did not reveal all the significant features of the behaviour of MgO in this respect. A full and complete picture of the facts is clearly necessary before it is possible for their real significance to emerge. It was with a view to fill the lacunae in the published results of Burstein, Oberly and Plyler that the present experimental research was undertaken.

2. Some general considerations

In the spectrographic investigations with cleavage plates, we are interested in determining the percentage of transmission through the plate and of ascertaining the spectral composition of the transmitted radiation and the manner in which it varies with the thickness of the plate. The loss in transmission may be divided into three parts: (a) the loss by reflection at the surface of incidence, (b) the loss by absorption within the material and (c) the loss by reflection at the surface of emergence. The relative proportions of these three losses would evidently vary with the circumstances, including especially the thickness of the plate, as this would determine the magnitude of the true absorption loss. When the reflecting power is large, the three losses would add up and it would become difficult to extricate them from each other and evaluate them separately.

At wavelengths greater than $13\ \mu$, the reflecting power of MgO is small, as was shown by Burstein, Oberly and Plyler, and its alteration with wavelength would therefore not be significant. Hence in the spectral region between $5\ \mu$ and $13\ \mu$ covered by their studies of the transmission by MgO, the interpretation of the observations presents no particular difficulty. The position is, however, different in the wavelength range between $13\ \mu$ and $15\ \mu$ in which the reflecting power was shown by Burstein *et al.* to rise steeply from nearly zero to 75%. This rapid increase would make it difficult to determine how the absorption loss within the material varies with wavelength in the same range. However, by making observations with different thicknesses, the existence of a true absorption could be

demonstrated. The position would be much more difficult in the wavelength range between $15\ \mu$ and $25\ \mu$. The reflecting power in this range is very high and hence the percentage transmission would be small and difficult to determine, unless indeed the plate is itself so thin that the full reflecting power would be unable to manifest itself. Indeed, it is clear that for an elucidation of the infra-red behaviour of MgO in the wavelength range between $15\ \mu$ and $25\ \mu$, it would be necessary to work with extremely thin layers of the material, not exceeding a few microns.

A method of obtaining MgO films for the study of their transmission properties which has been frequently employed by the earlier investigators is that of the deposition of the fumes of burning magnesium on a plate transparent to infra-red radiation. It will suffice here to refer to the work of A O Momin published in these *Proceedings* in which references to the earlier literature will be found (*Proc. Indian Acad. Sci.*, 1953, A37, 254). Momin made a series of measurements with fourteen different thicknesses of MgO films prepared by fuming on to a KCl plate from a burning magnesium ribbon. Commencing with an extremely thin layer which was just visible, the thickness was progressively increased by adding more layers of MgO on the same plate by fuming up to a thickness of about 2.4 millimetres when the films begin to break away from the KCl plate. The readings were taken with a single-beam Beckman Model IR 2 infra-red spectrophotometer making point-to-point observations. Four typical graphs which between them cover the whole range of thicknesses employed have been reproduced with Momin's paper. They show some interesting features, but it is quite clear on an inspection of the graphs that they do *not* represent the real transmission curves of MgO at any of the thicknesses used and that on the other hand they depict a complex effect in which the scattering of infra-red radiation in its passage through the optically heterogeneous film produced by the deposition of the fumes and the extinction produced by such scattering play a highly important role.

The spurious and misleading nature of the results given by fumed films of MgO becomes evident when it is remarked that to exhibit an observable transmission in the wavelength range between $15\ \mu$ and $25\ \mu$, the thickness of the film cannot exceed a few microns. Films of this order of thickness should be fully transparent in the wavelength range between $1\ \mu$ and $13\ \mu$. Actually, Momin's graph for his thinnest film shows a transmission of only 17% at $1\ \mu$. This increases fairly rapidly to 70% at $5\ \mu$ and then more slowly to 80% at $13\ \mu$. The optical heterogeneity of the film has thus a notable effect on its transmission up to $13\ \mu$. Hence, to assume that it would cease to influence the behaviour of the film at still greater wavelengths is clearly unjustifiable. The falsity of the assumption is demonstrated by the comparative studies made at this Institute with fumed MgO films and with two other techniques presently to be described. The publications by earlier investigators who have based themselves and their theoretical discussions on the results obtained with fumed MgO films are vitiated by this error and are therefore entirely valueless.

3. Methods of the present investigation

Since MgO crystals exhibit an easy cleavage parallel to the cube faces, it is possible to obtain a whole series of plates suitable for the observation and of various thicknesses ranging from several millimetres down to about a tenth of a millimetre. It is desirable to use a fairly large crystal to start with. The area of the plates detached from it would then be sufficient to make a satisfactory recording of the transmission curves. The cleavage surfaces are not always optically as smooth as could be desired. It is necessary in such cases to grind and polish both the faces to as high a degree of optical perfection as practicable. To obtain plates thinner than about a tenth of a millimetre, two alternative techniques are available. That employed in the present investigation was to grind and polish both faces of a cleavage plate about a millimetre thick to start with and having made observations with it, to grind one of the faces with the finest grade of carborundum abrasive until the thickness is reduced to the extent desired. The ground face is then repolished and the transmission recorded. This process can be repeated and the transmission by plates which are progressively thinner and thinner can be studied until the practical limit to the applicability of the method is reached. This limit is set by the fragility of the material. With plates of fair size, it is possible to reduce the thickness to about 50 microns, while with smaller sizes one can go down to about 20 microns.

An alternative technique is to immerse a cleavage plate in hot concentrated hydrochloric acid and allow the acid to act until the thickness of the plate has been reduced to the desired extent. The defect of this technique is the unsatisfactory nature of the resulting surfaces.

To obtain the extremely thin absorption layers with which one could expect to find an observable transmission in the spectral range between $15\ \mu$ and $25\ \mu$, the following technique was adopted in the present investigation. A small fragment of an MgO crystal was reduced to the finest possible state of subdivision by prolonged grinding in an agate mortar. A little of the material thus obtained was stirred up into a thin paste with liquid paraffin. The transmission in the KBr range of the spectrograph by the thinnest possible layer of this paste held between two KBr plates was recorded, the absorption by the paraffin being compensated by a similar layer of the liquid alone held between two KBr plates. As a test of the satisfactory nature of the technique, the transmission in the NaCl range was also recorded.

Another technique which was also adopted was to mix a very small quantity of very finely divided MgO with one gram of finely powdered KBr and to compress the MgO–KBr mixture under high pressure in a vacuum into a flat tablet of which the transmission was recorded. By varying the quantity of MgO which was put into the tablet, the effective absorption path could be increased to the extent desired.

Since the paste and pellet techniques gave very similar results, it was not

considered necessary to try out still another possible procedure of obtaining thin films of MgO, viz., that of evaporating the material in a vacuum and depositing it on a suitable support.

4. Review of the results

The wavelength scale of the recording spectrograph for the NaCl optics covers the range between $1\ \mu$ and $15\ \mu$, while with the KBr optics it covers the range between $13\ \mu$ and $24\ \mu$. The overlap of the two scales over the range between $13\ \mu$ and $15\ \mu$ is a useful feature, since it provides a check on the proper functioning of the instrument and as it is also the range over which the reflecting power of MgO increases rapidly from nearly zero to some 75%.

Some 75 spectrographic records were made with the instrument, the majority with the NaCl optics and the rest in the KBr range. Some 25 different cleavage plates of various sizes and thicknesses were employed and numerous records were also obtained with the paste and pellet techniques already described. Before we proceed to discuss the results in detail, it appears useful to review the general features which emerge from the study, thereby enabling us to get a broad picture of the experimental situation and consider its significance.

The most striking feature exhibited by the records is that the infra-red behaviour of MgO is quite different in the three spectral ranges which we shall refer to as I, II and III respectively. Spectral range I extends from $6\ \mu$ to $10\ \mu$. Spectral range II extends from $10\ \mu$ to $15\ \mu$. Spectral range III extends from $15\ \mu$ to $24\ \mu$. Closely associated with this feature is the fact that the spectral character of the radiation transmitted by MgO depends greatly upon the absorption path. When the cleavage plate is a few millimetres thick, spectral region I exhibits a progressive change from complete transparency at $6\ \mu$ to complete opacity at $10\ \mu$, while spectral regions II and III are completely cut out. If the absorption path is a few tenths of a millimetre, spectral range I is almost completely transmitted and spectral region II exhibits a transmission spectrum with characteristic features, while spectral region III is cut out. If the absorption path is only a few microns, spectral region III exhibits an observable transmission, while spectral region I is completely transmitted and spectral region II is let through for the most part.

The facts stated above clearly indicate that the infra-red activities which manifest themselves respectively in the spectral regions I, II and III are of very different orders of magnitude. An explanation for this situation which suggests itself is that the same fundamental modes of vibration are responsible for the activities manifested in the three spectral regions, but that we are concerned with the fundamental modes and with their first and their second overtones respectively in the three cases. In other words, the fundamental absorption frequencies manifest themselves in spectral region I, their first harmonics in the spectral region II and their second harmonics in spectral region III. On this basis,

the great differences in the strength of the observed absorptions in the three regions would find an immediate explanation.

If what has been suggested above is correct, we should expect to find quantitative relationships between the specific features observed in the spectral regions I, II and III in the recorded transmission curves. We proceed, therefore, to describe and discuss these observed features.

5. Spectral region I: $6\ \mu$ to $10\ \mu$

We may begin with a few remarks on the transmission of infra-red radiation in the wavelength range between $1\ \mu$ and $5\ \mu$ by cleavage plates of MgO. Residual imperfections in the cleavage surfaces are unavoidable. Their effect manifests itself as a diminution in the percentage of the regularly transmitted radiation in the region of the near infra-red. If, however, a large-sized crystal is used and its cleavage is effected with due care, the effect of surface imperfections on the transmission which may be perceptible at $1\ \mu$ becomes small at $4\ \mu$ and negligible at $5\ \mu$. Transmissions as high as 95% may be obtained at $5\ \mu$.

The region between $5\ \mu$ and $6\ \mu$ is of particular interest. With a cleavage plate 7.5 millimetres thick, the transmission is observed to diminish by 8% between $5\ \mu$ and $6\ \mu$. With a plate thickness of 3 millimetres, the diminution is only 3%, while with a plate thickness of 1.6 millimetres, there is no observable fall of the transmission between $5\ \mu$ and $6\ \mu$, the curve running quite horizontally between these wavelengths. It is clear from these observations that while there is a sensible absorption of infra-red radiation between $5\ \mu$ and $6\ \mu$, it is extremely weak and of a lower order of magnitude than the absorption between $6\ \mu$ and $10\ \mu$ which we shall proceed to describe and discuss.

Figure 1 reproduces the record obtained with a cleavage plate 2.34 millimetres thick. We may draw attention here to the following features observed in it. The record runs horizontally between $5\ \mu$ and $6\ \mu$. Beyond $6\ \mu$, it dips down and becomes steepest at $6.8\ \mu$. It then takes a sharp turn and follows a different course in which the wavelength at which the transmission drops most steeply is $7.85\ \mu$. Between $8\ \mu$ and $9\ \mu$ the curve again changes its course. The slope is rather small at $8.5\ \mu$, beyond which it increases rapidly. The wavelength of steepest descent is $9\ \mu$. Between $9\ \mu$ and $10\ \mu$, the curve descends less quickly. Its slope diminishes until finally the curve touches the line of zero transmission at $10\ \mu$. Beyond $10\ \mu$, there is a complete cut-off.

Thus, the spectrographic record of transmission between $6\ \mu$ and $10\ \mu$ consists of three distinct sectors which exhibit quite different features, the transmission falling most steeply in the three sections at the wavelengths $6.8\ \mu$, $7.85\ \mu$ and $9\ \mu$ respectively. The three sectors can also be recognised in numerous other records which have been made with various thicknesses, viz., 7.5 mm, 3 mm, 1.6 mm, 1.34 mm, 1.04 mm and 1 mm. It has, however, not been thought necessary to

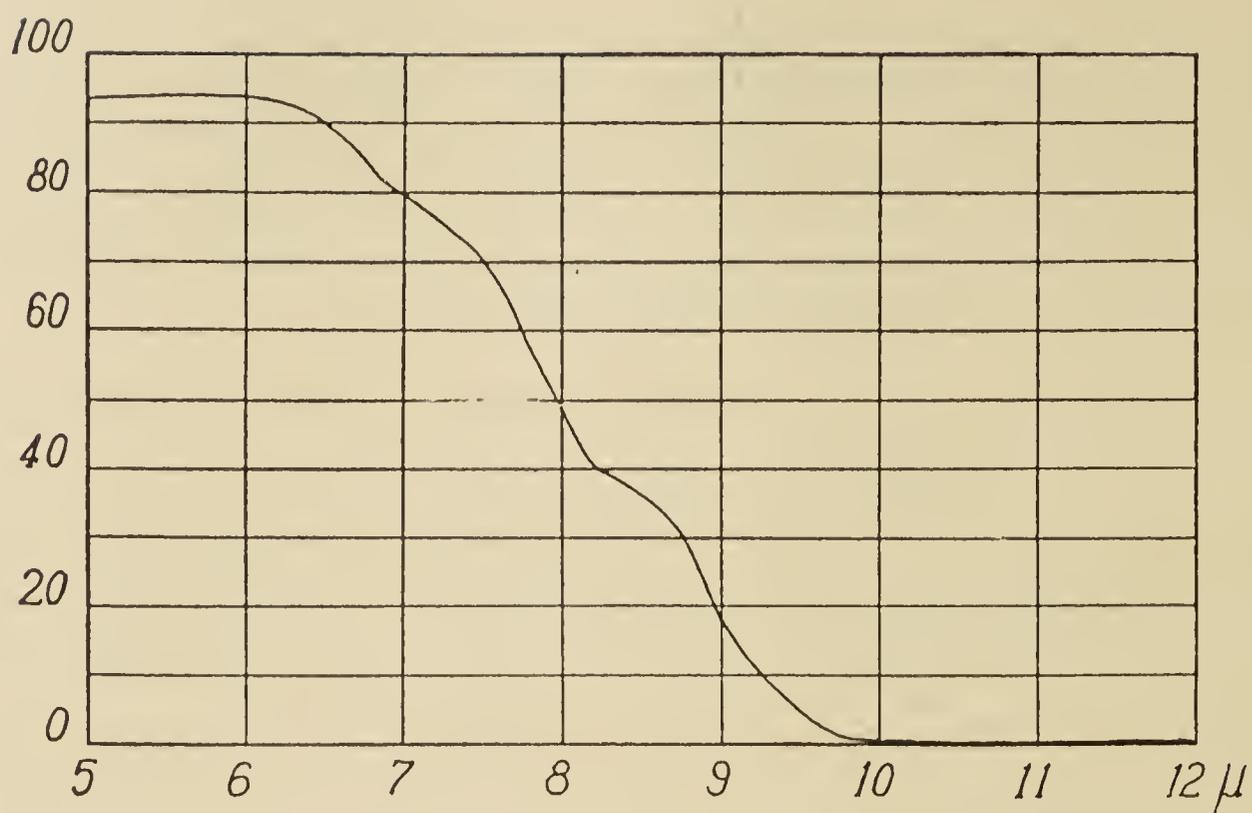


Figure 1. Transmission by an MgO plate 2.34 mm thick.

reproduce all these records here. That the three sectors exhibit the effect of specific absorptions is shown by the fact that each of them has a distinct absorption strength and that this results in altering the overall configuration of the graph in the wavelength range between 6μ and 10μ when the thickness is increased or diminished. Nevertheless, there is no difficulty in recognising the individual distinctive features described above in every case. In particular, the wavelengths of steepest descent, viz., 6.8μ , 7.85μ and 9μ , remain the same in all the records. Thus, these wavelengths possess a real significance in relation to the absorptive behaviour of MgO.

The wavelengths 6.8μ , 7.85μ and 9μ correspond to infra-red frequencies which expressed in wave-numbers are respectively 1470 cm^{-1} , 1275 cm^{-1} and 1110 cm^{-1} . Assuming these to be the second overtones of a set of fundamentals, the latter would be 490 cm^{-1} , 425 cm^{-1} and 370 cm^{-1} in wave-numbers and 20.40μ , 23.52μ and 27μ respectively in wavelengths. The first overtones would then have the frequencies 980 cm^{-1} , 850 cm^{-1} and 740 cm^{-1} in wave-numbers and the corresponding wavelengths would be 10.2μ , 11.76μ and 13.5μ . The frequencies of the fourth order would be 1960 cm^{-1} , 1700 cm^{-1} and 1480 cm^{-1} and the corresponding wavelengths 5.1μ , 5.9μ and 6.8μ respectively. We give below a table of these frequencies and wavelengths.

The figures listed in table 1 enable us immediately to explain various facts already known regarding the infra-red behaviour of MgO. For example, Burstein, Oberly and Plyler had observed that the reflecting power of MgO determined and represented graphically is highest in the wavelength region between 20μ and 24μ . We notice that this region includes the first two fundamental wavelengths shown in table 1. Then again, Burstein, Oberly and

Table 1. Vibrational frequencies and corresponding wavelengths

Order	Frequencies in cm^{-1}	Wavelengths in μ
Fundamental	490, 425, 370	20.4, 23.52, 27
Octave	980, 850, 740	10.2, 11.76, 13.5
Third Harmonic	1470, 1275, 1110	6.8, 7.85, 9
Fourth Harmonic	1960, 1700, 1480	5.1, 5.9, 6.8

Plyler had noticed that in the transmission curves of MgO plates which were less than a millimetre thick, two well-defined absorption maxima appear whose wavelengths were given by them as 10.19μ and 11.82μ . These may be identified as the first two wavelengths of the octave series shown in table 1. The fact mentioned earlier in the present memoir, that there is an extremely weak infra-red absorption between 5μ and 6μ is also satisfactorily explained, since the first two wavelengths shown as the fourth harmonics in table 1 fall within this range. Thus, what is already known regarding the infra-red behaviour of MgO provides us with ample justification for accepting the basic idea which was put forward above and making use of it in interpreting the fresh experimental data which emerge from the present investigation.

6. Spectral region II: 10μ to 15μ

That the infra-red absorption appearing between 6μ and 10μ is of a higher order than that manifested between 10μ and 15μ is clearly proved by various facts of observation. In the first place, there is a total cut-off between 10μ and 15μ unless the absorption paths used are much smaller than those which are required to exhibit any sensible absorption in the 6μ to 10μ region. Then again, when such smaller thicknesses are used, the transmission is observed to be nearly complete over the range between 6μ and 10μ ; in these circumstances also, a steep fall is observed in the transmission curve near 10μ which is the dividing boundary between spectral ranges I and II (see figures 2, 3, 4 and 5).

On the long-wave side of the boundary between spectral regions I and II, the characteristic absorption at 10.20μ first clearly makes its appearance when the absorption path is rather less than one millimetre. This absorption evidently represents the octave of the highest fundamental frequency of vibration of the crystal structure of MgO. As the absorption path is progressively diminished, this absorption emerges more and more clearly from its background and becomes a very striking feature of the transmission curves. Its initial appearance is shown in figure 2 which was recorded with a cleavage plate 0.91 mm thick. A later stage in which the absorption at 10.2μ is very prominent and exhibits its characteristic

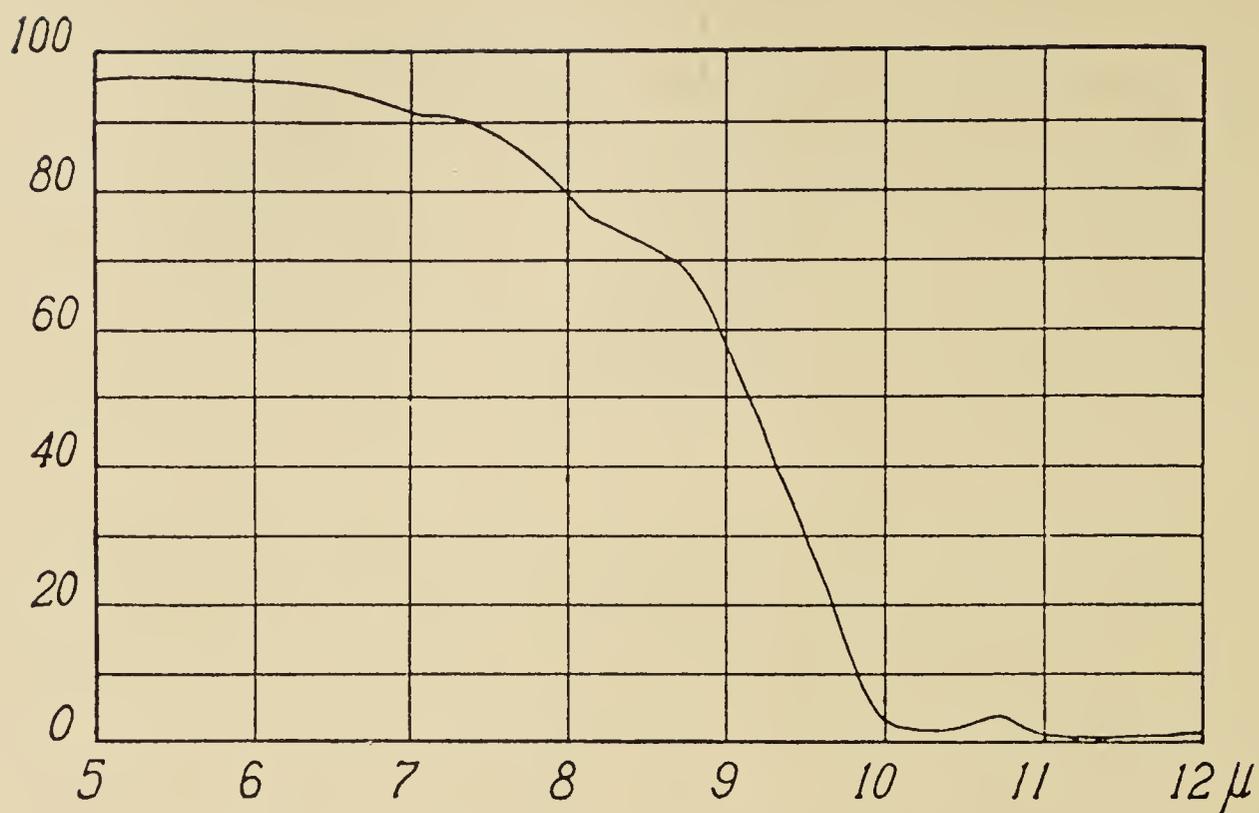


Figure 2. Transmission by an MgO plate 0.91 mm thick.

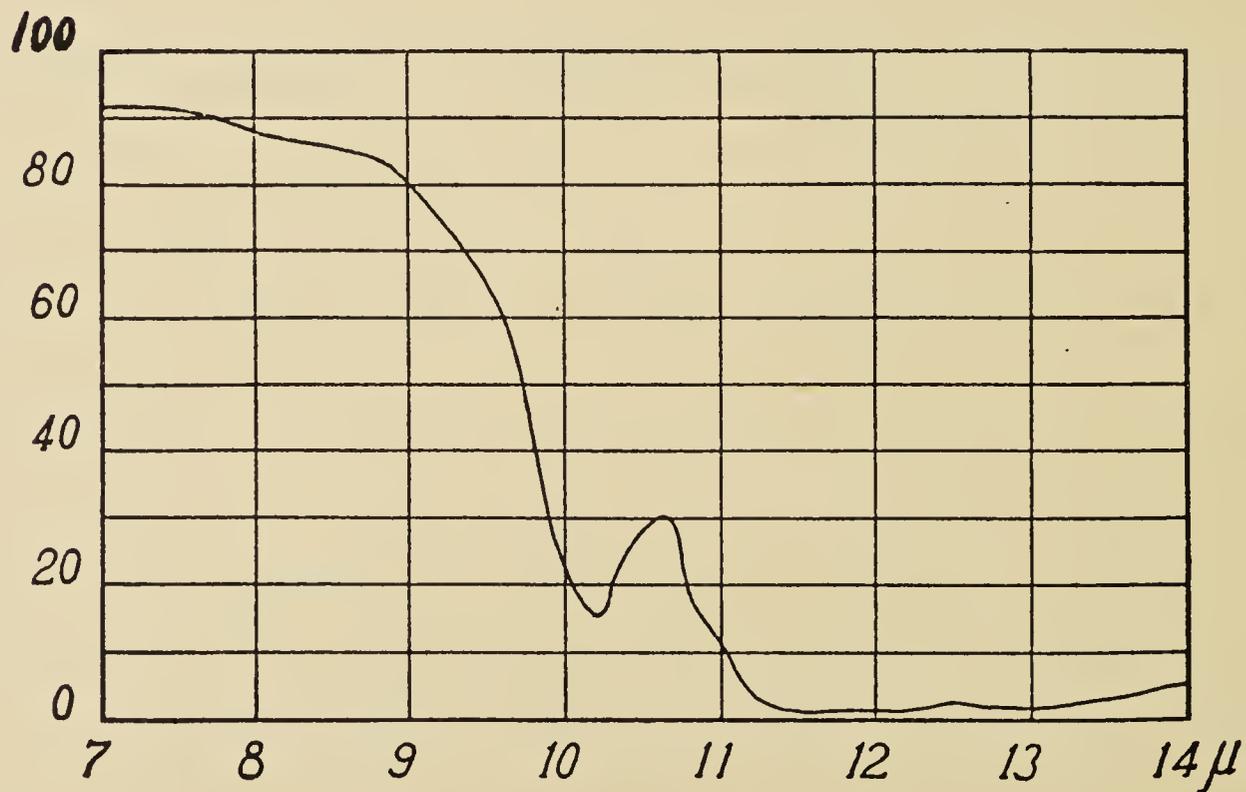


Figure 3. Transmission by an MgO plate 0.3 mm thick.

sharpness and V-shaped configuration is represented in figure 3 recorded with a cleavage plate 0.3 mm thick. With diminishing thickness of the plate, the V-shaped dip in transmission retains both its sharpness and its position on the wavelength scale at 10.2μ but moves upwards in the figure, as is to be expected from the diminishing strength of the absorption which it represents (see figures 4, 5, 6, 7, 8 and 9).

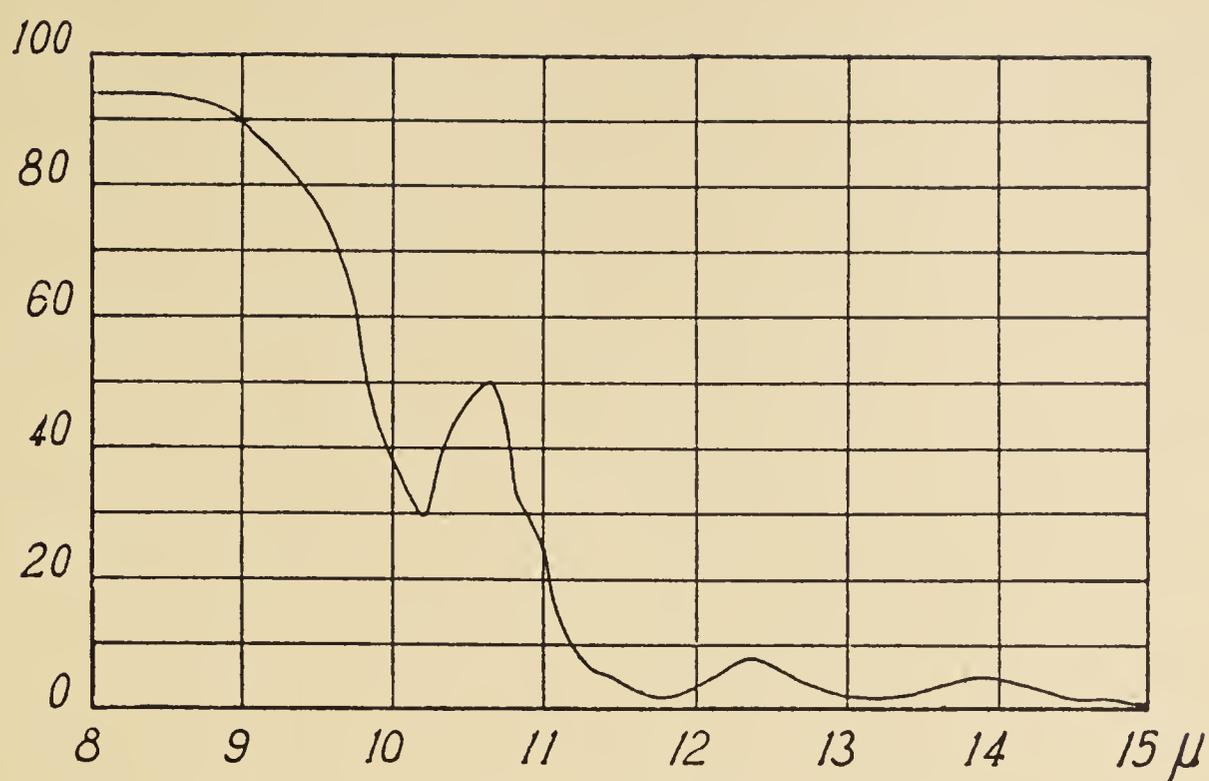


Figure 4. Transmission by an MgO plate 0.128 mm thick.

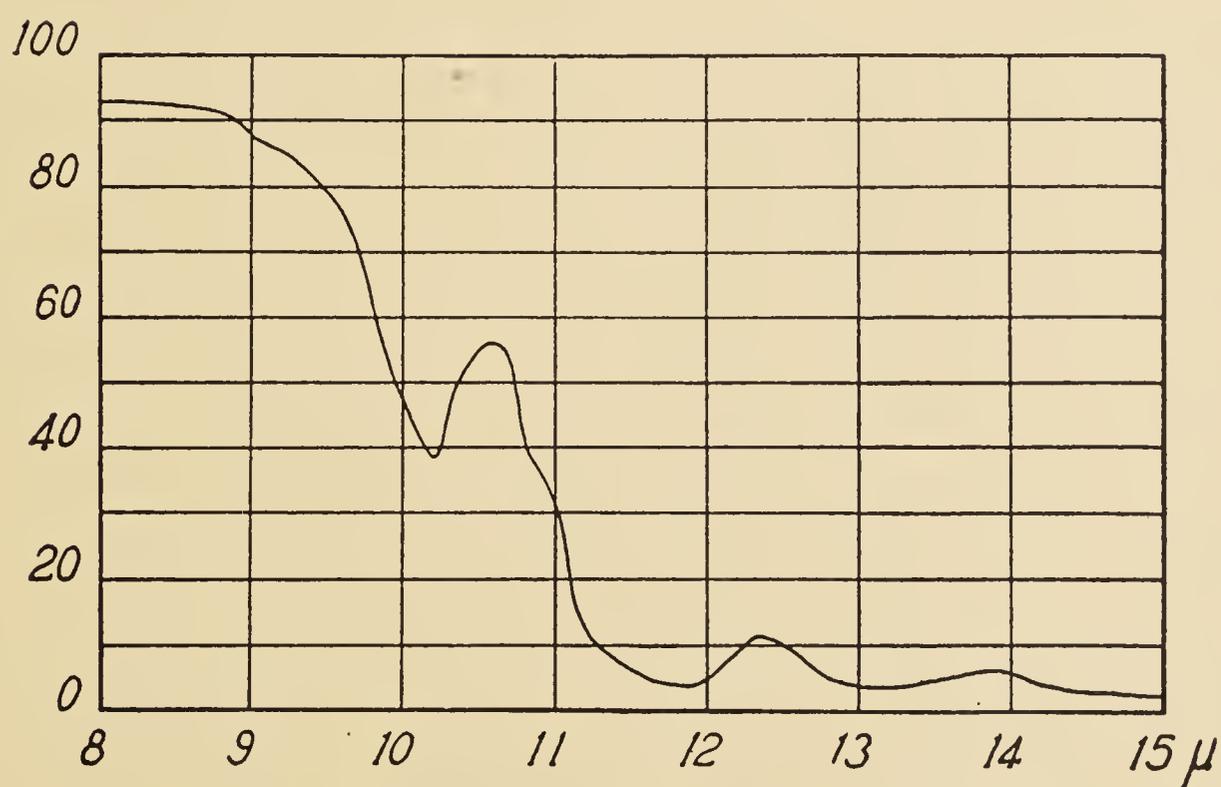


Figure 5. Transmission by an MgO plate 0.114 mm thick.

The second minimum of transmission located at 11.76μ and shown in table 1 as an octave of a fundamental mode makes its appearance rather inconspicuously in figure 3. But as the thickness of the plate is progressively diminished, it becomes more and more conspicuous, as will be seen from the series of records, until it becomes even more conspicuous than the minimum at 10.2μ (figures 4, 5, 6, 7 and 8). Like the minimum at 10.2μ , the minimum at 11.76μ retains its position on the wavelength scale but moves upwards as the absorption path is diminished.

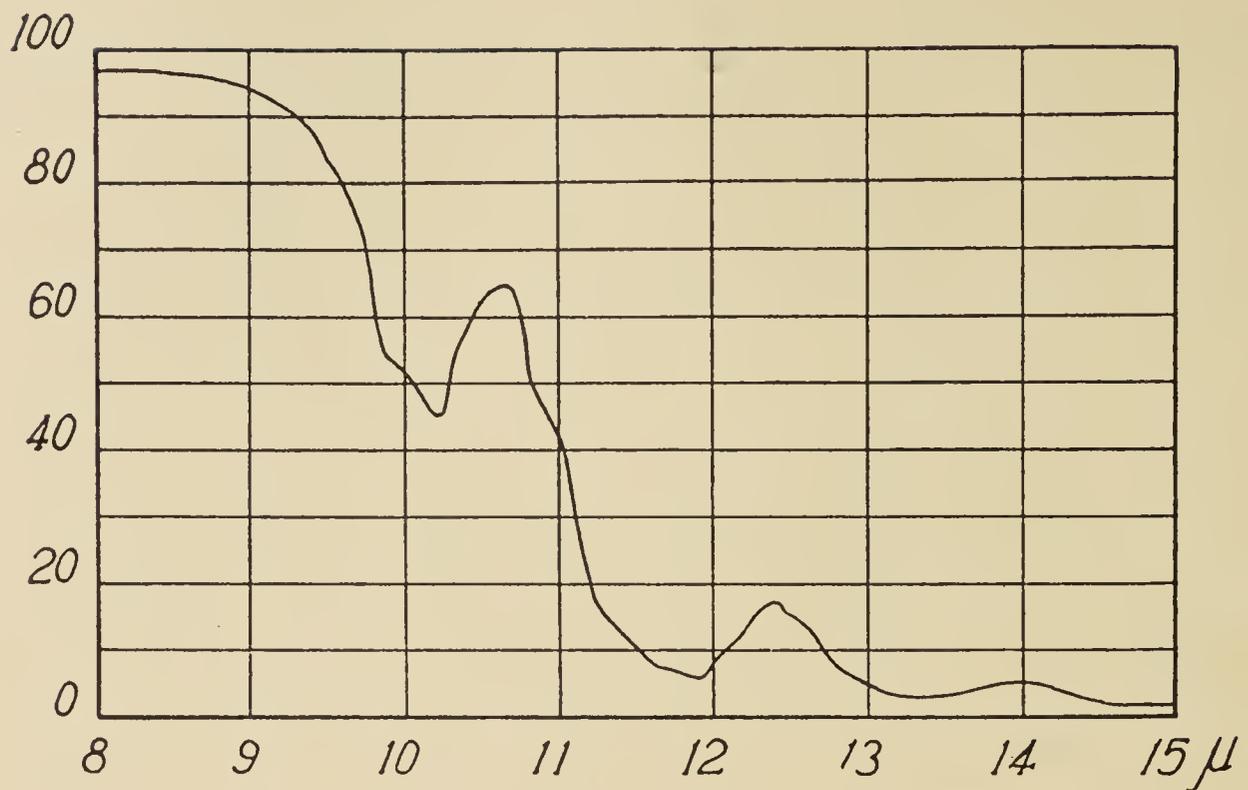


Figure 6. Transmission by an MgO plate 0.088 mm thick.

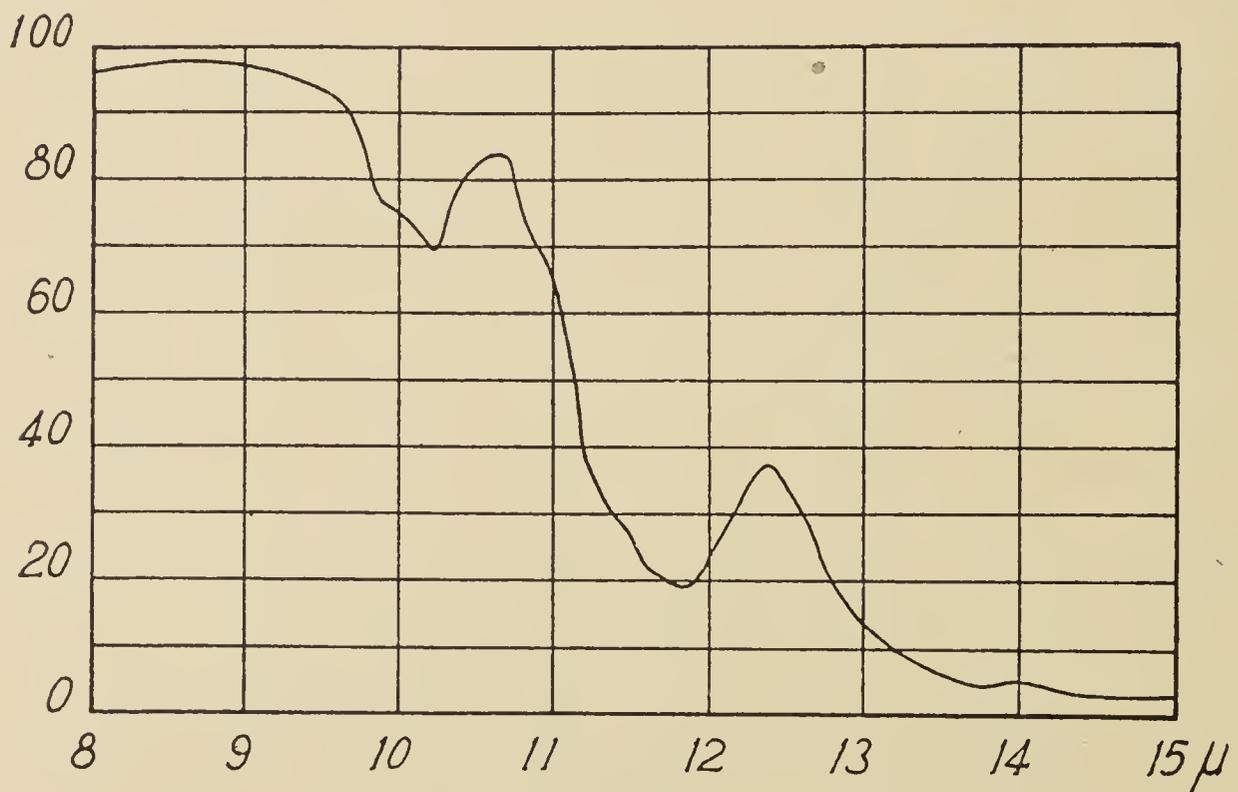


Figure 7. Transmission by an MgO plate 0.06 mm thick.

Referring to the spectrographic records reproduced as figures 4, 5 and 6, we find that in each of them, the transmission reaches a maximum at about 12.4μ and then drops down to a much lower value at about 13.3μ . The actual transmission at 13.3μ is small in figure 4 and is distinctly larger in figures 5 and 6. That there is a real absorption at 12.4μ and that this goes up to a much higher value at 13.3μ is thus abundantly clear. We are therefore justified in stating that there is a minimum of transmission at about the wavelength 13.5μ which was

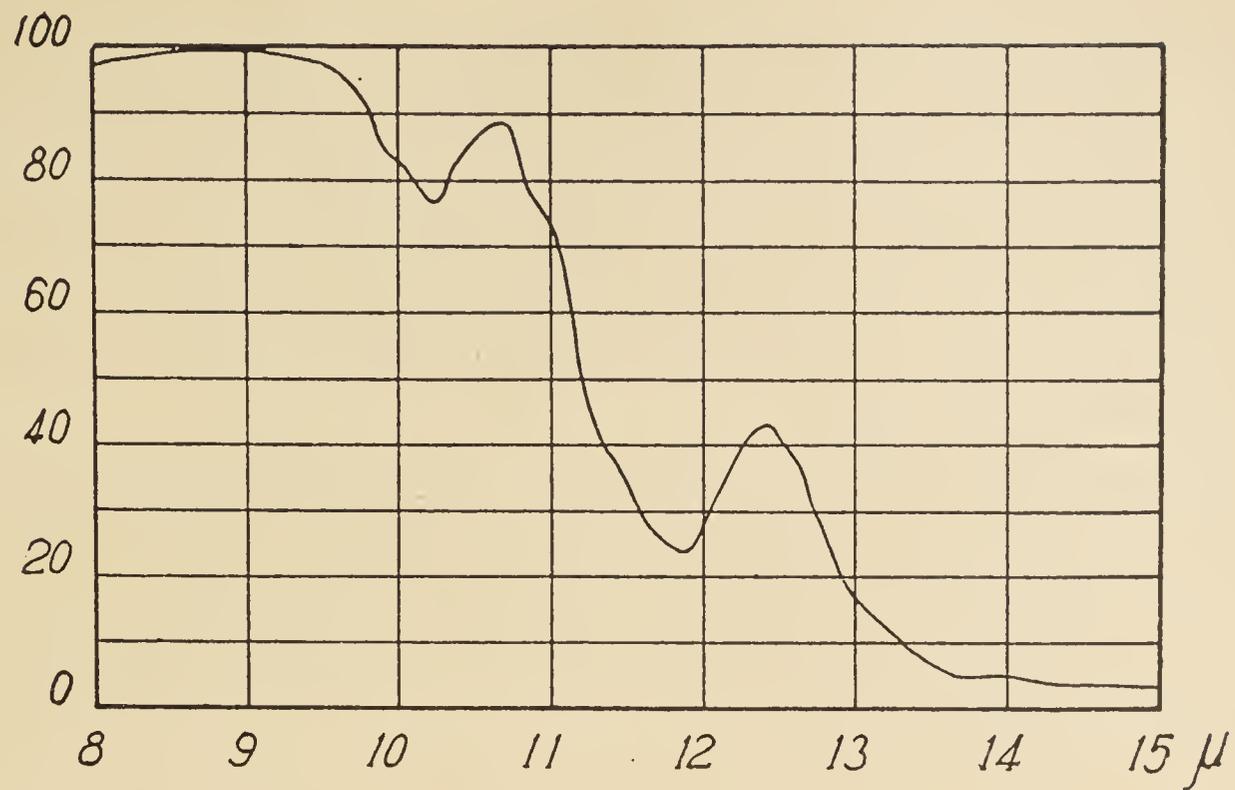


Figure 8. Transmission by an MgO plate 0.057 mm thick.

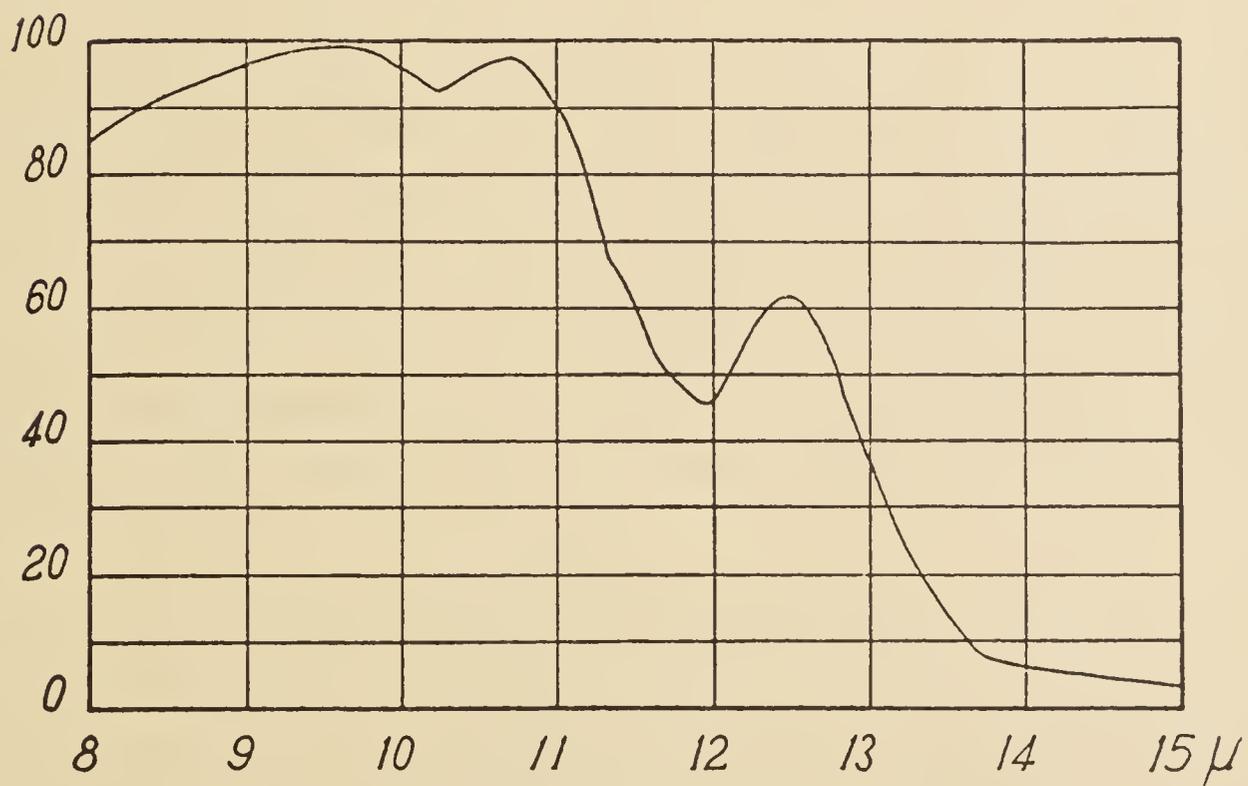


Figure 9. Transmission by an MgO plate 0.021 mm thick.

listed in table 1 as the third in the series of octaves. The reason why the existence of this minimum is not made more conspicuous by a progressive rise of the curve in the region between 13.5μ and 15μ with diminishing thickness is to be found in the enormous increase in the reflecting power of MgO which occurs in the same region of wavelength. The fall in transmission arising therefrom more than sets off the increase in the transmission due to the diminishing thickness of absorbing material.

That the percentage transmission through a plate of MgO in the wavelength region between $13.7\ \mu$ and $15\ \mu$ is almost entirely determined by the reflection losses is evident on a comparison of the records for this region appearing in figures 8 and 9. The absorbing path in the two cases was respectively 57 microns and 21 microns. It will be noticed that in spite of this great difference in the thickness of the absorbing material, the percentage transmission between $13.7\ \mu$ and $15\ \mu$ remains substantially unaltered, whereas between $12\ \mu$ and $13.7\ \mu$, it has increased enormously.

Thus, the inference from the observations made in spectral region I that three absorptions which we now locate at $10.2\ \mu$, $11.82\ \mu$ and $13.7\ \mu$ respectively should appear in spectral region II is abundantly confirmed by the actual facts of observation. The conclusion follows irresistibly that the MgO crystal structure has the three fundamental modes of vibration with the respective frequencies which have been listed in table 1.

7. Spectral region III: $15\ \mu$ to $24\ \mu$

The techniques used to study the transmission in this region using the KBr optics have already been explained. Figure 10 shows two transmission records obtained with the paste technique: the upper of the two curves was obtained without any spacer to hold apart the two KBr plates between which the thin film of paraffin containing the finely divided MgO was located. The thickness of the film was hence the very smallest possible and presumably of the same order of magnitude as the size of the MgO particles contained in it. The second record in the figure was with a spacer 30 microns thick separating the two KBr plates. The two records reproduced in figure 11 are those recorded with NaCl optics for the

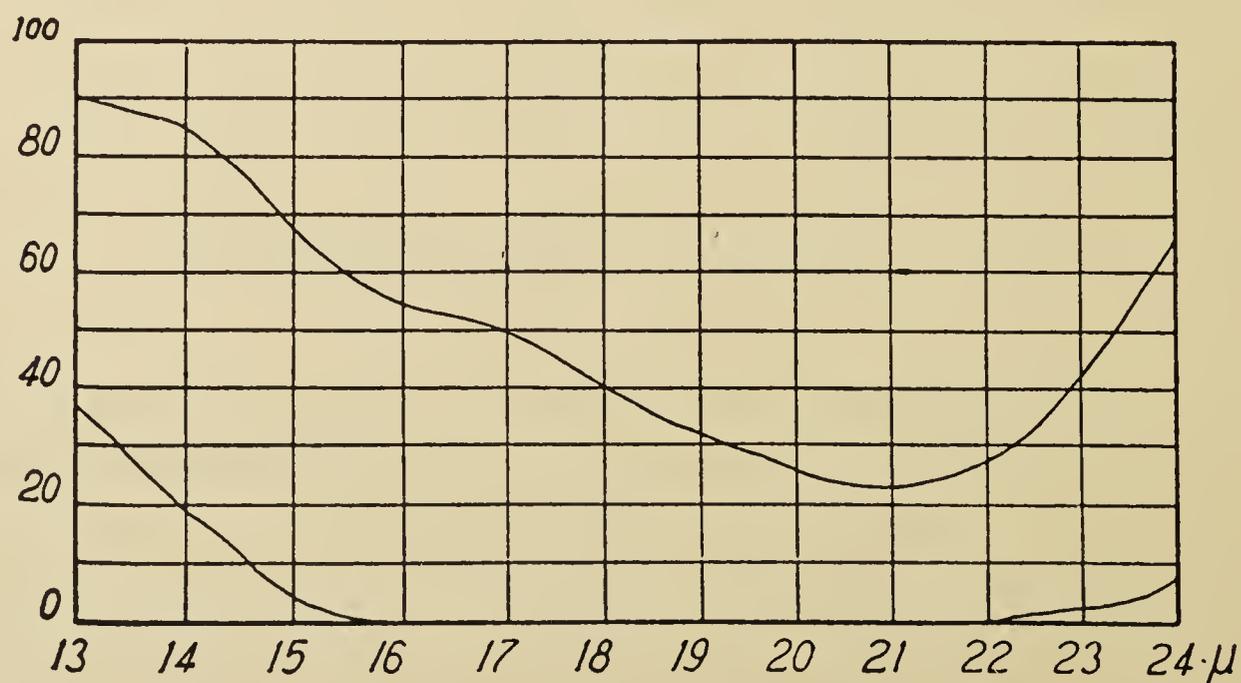


Figure 10. Transmission curve of MgO films (paste technique).

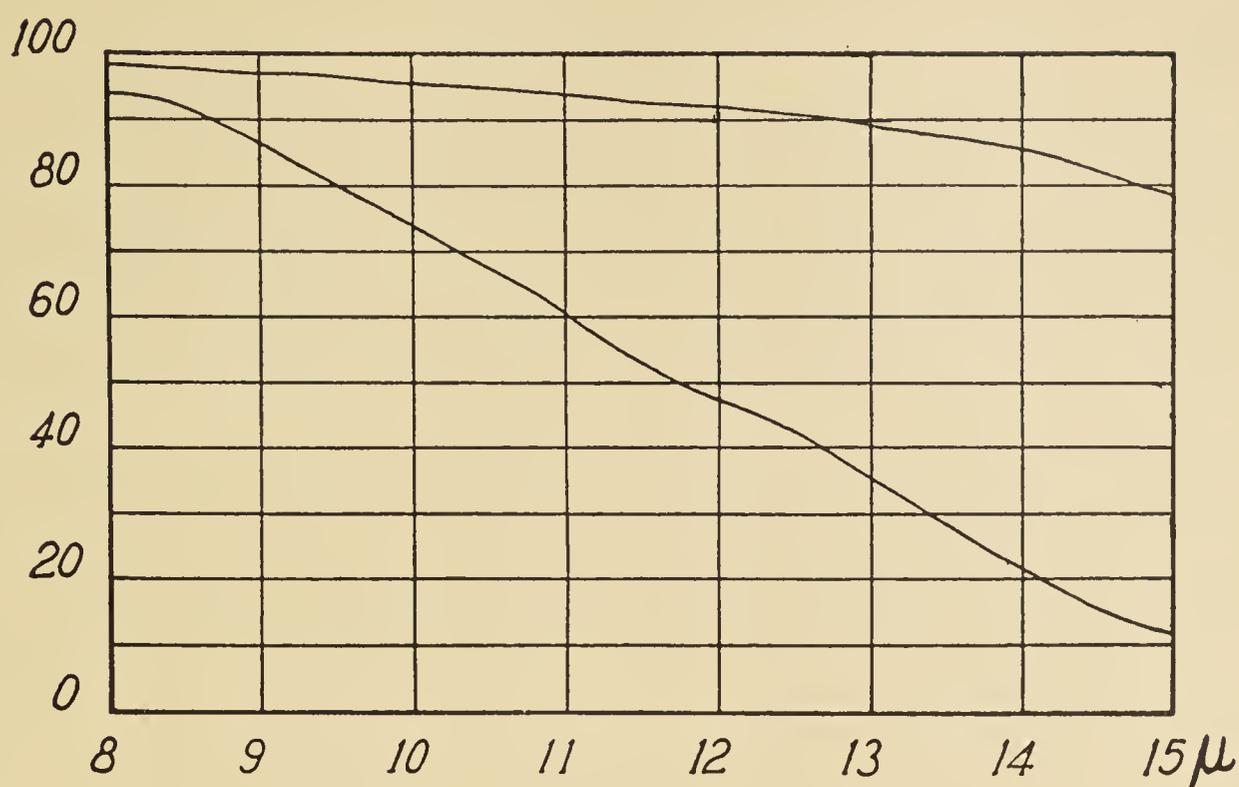


Figure 11. Transmission curve of MgO films (paste technique).

wavelength region between $8\ \mu$ and $15\ \mu$ in the same two cases. We shall return presently to a consideration of the features appearing in figures 10 and 11.

Figure 12 below reproduces four records for the KBr range of the spectrograph obtained with the pellet technique already described. The pellet was a circular disc of 1 centimetre radius containing one gram of KBr and four different quantities of finely divided MgO, viz., 1 milligram, 1.2 milligrams, 2 milligrams and 5 milligrams respectively. The effective absorption paths through MgO would thus be respectively in the four cases $3.2\ \mu$, $3.8\ \mu$, $6.4\ \mu$ and $16\ \mu$. As is to be expected, the four records exhibit a rapid and progressive change as the effective thickness of the MgO layer is increased.

We may make the following remarks on the data presented in figures 10, 11 and 12. It is evident that the results obtained with the two different techniques are very similar and that they fit into each other perfectly when the differences in the effective absorption paths are taken into consideration. Indeed, the curves in figures 10 and 12 form a regular sequence showing how the transmission alters with a progressive increase in absorption path. The upper curve in figure 10 represents the behaviour of the thinnest possible layer; the first three curves in figure 12 represent the subsequent alterations with increasing thickness, while the second curve in figure 10 and the fourth curve in figure 12 represent the final stages in which the layers are practically opaque to all radiations in the wavelength region between $15\ \mu$ and $24\ \mu$.

The first of the two curves reproduced in figure 10 is particularly important. It depicts the absorptive behaviour of an MgO film when it is so thin that the losses due to reflection at its two surfaces can be disregarded. It is significant that the

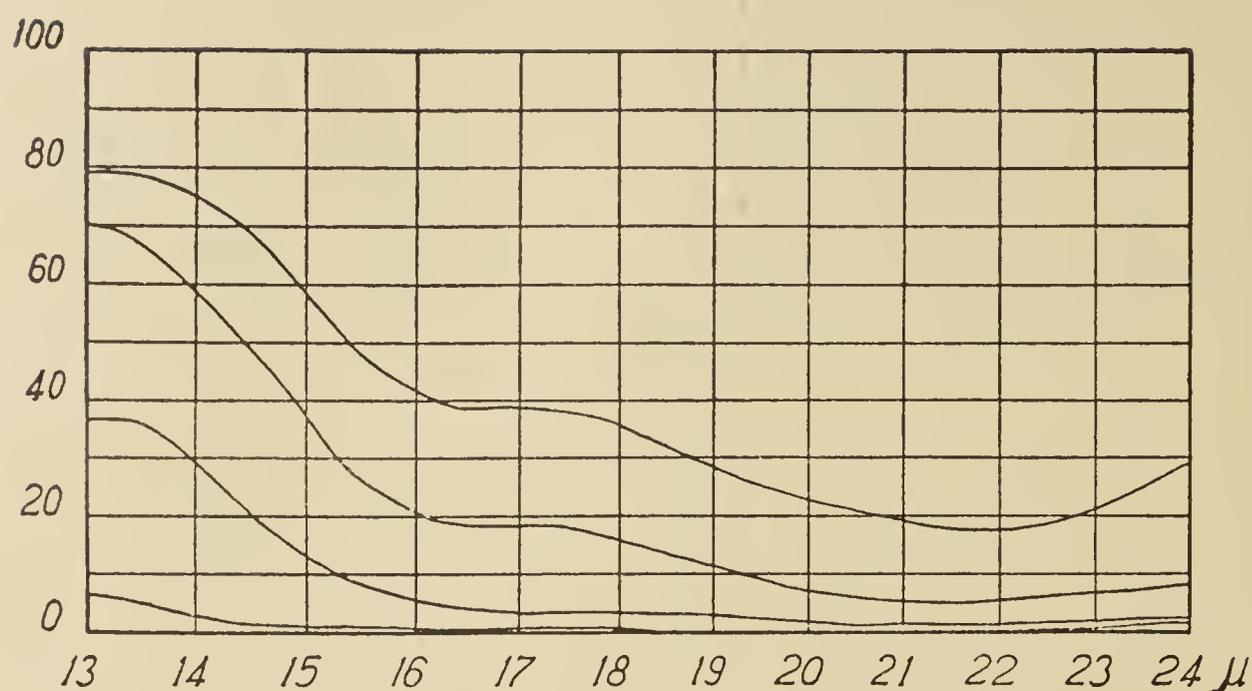


Figure 12. Transmission curve of MgO films (pellet technique).

absorption is greatest at about $21\ \mu$ and falls off quickly at greater wavelengths. This is the behaviour which we might expect to observe if the fundamental mode of highest frequency of which the characteristic wavelength is $20.4\ \mu$ is the only mode which is infra-red active, while the numerous other modes whose characteristic wavelengths are larger and have been listed in table 1 are either totally inactive or active only in a very minor degree. The shift of the maximum from the theoretical value $20.4\ \mu$ to the observed value of $21\ \mu$ is readily understood on that basis.

The two curves reproduced in figure 11 are also highly significant. They show that the films studied were completely transparent at $8\ \mu$. The two upper curves in figure 10 and in figure 11 respectively agree in showing a transmission of 90% at $13\ \mu$ while the two lower ones similarly agree in showing a transmission of 35% at $13\ \mu$. The transparency of the films at $8\ \mu$ is an indication that the losses due to scattering at all greater wavelengths are negligible. In other words, it is a demonstration of the satisfactory nature of the technique employed. In this respect, the results provide a very striking contrast with the behaviour of fumed MgO films. As has already been remarked, the fumed MgO films exhibit the effect of scattering very markedly. Hence the results obtained with them are erroneous and totally misleading.

We may also remark on a feature shown by the upper curve in figure 10 and also by the two upper curves in figure 12, viz., the downward bulge of the transmission curve in the region of wavelengths between $15\ \mu$ and $17\ \mu$. This is a clear indication that there is a specific absorption which we shall locate at $16\ \mu$ and which is clearly the octave of still another fundamental mode whose characteristic wavelength is $32\ \mu$ and characteristic frequency is therefore $313\ \text{cm}^{-1}$.

8. Summary

Records have been made of the infra-red absorption spectra between $5\ \mu$ and $24\ \mu$ of magnesium oxide in the form of polished cleavage plates of various thicknesses ranging from 7.5 millimetres down to 20 microns. Films with an effective absorption path ranging from 1 micron to 16 microns have also been prepared by two different techniques and studied. They give results in close agreement with each other.

A critical comparative study of the data reveals that the infra-red absorption by MgO has its origin in a set of distinct modes of vibration of the crystal structure possessing discrete frequencies. The highest of these frequencies corresponds to an infra-red wavelength $20.4\ \mu$. It is strongly active as a fundamental and also as overtones. The infra-red absorption spectra enable us to recognize the presence of three other modes with lower frequencies which are inactive as fundamentals but are strongly active as overtones. The characteristic frequencies of MgO (including the highest) revealed by the investigation are respectively in wave-numbers $490\ \text{cm}^{-1}$, $423\ \text{cm}^{-1}$, $365\ \text{cm}^{-1}$ and $313\ \text{cm}^{-1}$. The corresponding wavelengths are $20.4\ \mu$, $23.64\ \mu$, $27.4\ \mu$ and $32\ \mu$.

The present investigation shows that the results reported earlier by other authors which were obtained with fumed MgO films are spurious and hence that all theoretical discussions based thereon are valueless.

The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part II. Dynamical theory

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1. Introduction

The fundamental property of the atomic structure of a crystal is that it comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Hence the normal modes of atomic vibration characteristic of the structure of a crystal should satisfy a similar requirement; in other words, they should remain unaltered following such a unit translation. From this, it follows that the atomic modes of vibration satisfy the following rule: in any normal mode, equivalent atoms in the structure have *either* the same amplitude and the same phase, *or* the same amplitude but alternating phases, along the axes of the lattice. In the MgO structure, we have two interpenetrating face-centred cubic lattices of Mg and O atoms respectively. Applying the rule stated, it should be possible to deduce the normal modes of vibration of this structure purely from symmetry considerations. One could also go further and obtain explicit formulae for the frequencies of the normal modes in terms of the interatomic force-constants. We shall, in what follows, carry out the programme here indicated.

2. Vibrations of a face-centred cubic lattice

The three unit translations in a face-centred cubic lattice are parallel to the three edges of the primitive rhombohedral cell of the lattice. These edges are found by joining an atom at a cube corner with the three atoms at the centres of the three adjoining cube faces. The various modes of normal vibration of the lattice given by the rule stated above are found by choosing one or another of the eight possible combinations of the phases of these three atoms relative to the phase of the atom at the cube corner and continuing the scheme to the more distant atoms in the lattice. It is then found that the possible modes of vibration may be described *either* as movements of the cubic planes of atoms in the crystal *or* as

movements of the octahedral planes of atoms; in either case, the alternation of phase along an axis results in the alternate planes of one or the other species moving in opposite phases. Since we have three sets of cubic planes and four sets of octahedral planes, the movements of these planes normal to themselves would give three and four normal modes respectively, but only two distinct frequencies. We have also to consider the movements of the planes parallel to themselves, and as there are two possible directions of movement in each case, we obtain six and eight such normal modes respectively, but here again only two additional frequencies by reason of the symmetry of the crystal. Thus, in all, we have only four distinct frequencies of vibration. In the foregoing we left out of consideration the case in which the phases of movement of the three atoms at the face-centres and of the atom at the cube corner are the same. This corresponds to a simple translation of the unit rhombohedral cell carrying eight atoms at its corners. The 24 degrees of freedom of movement of these eight atoms are thus distributed as follows amongst the possible movements of the lattice.

Table 1

	Degeneracy
Vibrations of the cubic planes normal to themselves	3
Vibrations of the cubic planes tangential to themselves	6
Vibrations of the octahedral planes normal to themselves	4
Vibrations of the octahedral planes tangential to themselves	8
Translations of the unit cell	3
Total degrees of freedom	24

3. The vibrations of the MgO structure

In the MgO crystal, the Mg and O atoms occupy the points of two similar face-centred cubic lattices interpenetrating each other. These are so disposed that each Mg atom is surrounded by six equidistant O atoms, and each O atom is surrounded by six equivalent Mg atoms. In the cubic planes of the structure the Mg and O atoms appear together, while in the octahedral planes they appear separately but in equidistant planes, each plane of Mg atoms having two planes of O atoms and each plane of O atoms having two planes of Mg atoms situated symmetrically on either side of it. This arrangement has interesting consequences regarding the possible vibrational modes of the structure, as we shall presently see.

Table 1 would represent equally well the schemes of vibration of the Mg atoms and of the O atoms. Hence, the interactions of these atoms with each other would result in a modification of the frequencies of vibration without altering the

geometry of the modes. Since the cubic planes contain both Mg and O atoms, each of their movements would split into two modes: in one of the two modes, the Mg and O atoms in a cubic plane would oscillate in the same phase and in the other they would oscillate in opposite phases. The situation would be a little different with respect to the atomic layers parallel to the octahedral faces. In view of the disposition of Mg and O atoms in these layers, it is evident that the oscillations of Mg and O layers would occur independently of each other, the Mg planes remaining at rest when the O planes oscillate and vice versa. The three translations of the unit cells would also split into two. The movement of the Mg and O atoms in opposite phases would give a triply degenerate normal mode, while their movement in the same phases would represent a residuum of three translations.

Thus, the structure would have only nine different frequencies of vibration, while the number of normal modes would be 45 which together with the residuum of the three translations would account for the 48 degrees of freedom of movement of 8 atoms of magnesium and 8 atoms of oxygen when added together. The description of the modes of vibration corresponding to each of the nine different frequencies is entered in the second column of table 2, while their respective degeneracies are shown in the third column of the table. These degeneracies are the same as shown in table 1, but they now total up to 48 instead of 24 as in the former table.

The modes have been shown in the first column of table 2 in the order of the magnitude of their respective frequencies suggested by the approximate formulae

Table 2

Sl. No.	Description of mode	Degeneracy
I	Oscillation of the Mg and O atoms in opposite phases	3
II	Tangential oscillations of the cubic planes, Mg and O atoms having opposite phases	6
III	Normal oscillations of the cubic planes, Mg and O atoms having same phases	3
IV	Normal oscillations of the octahedral planes of O atoms	4
V	Tangential oscillations of the octahedral planes of O atoms	8
VI	Normal oscillations of the octahedral planes of Mg atoms	4
VII	Tangential oscillations of the octahedral planes of Mg atoms	8
VIII	Normal oscillations of the cubic planes, Mg and O atoms having opposite phases	3
IX	Tangential oscillations of the cubic planes, Mg and O atoms having same phases	6
X	Translations	3
Total degrees of freedom		48

of the dynamical theory to be given presently. But this arrangement is subject to revision on the basis of a more accurate evaluation of those frequencies. It will be noticed that at the top of the table listed as mode I appears the triply degenerate oscillation of the Mg and O atoms in the structure moving against each other in opposition of phase. It will also be noticed that next to it in the descending order of frequency appear the tangential and normal modes of oscillation of the cubic layers of atoms. These are listed in the table as modes II and III, while two other modes of oscillation of the cubic layers in which the phases of movement of the Mg and O atoms are different appear at the bottom of the table as VIII and IX respectively. The oscillations of the octahedral layers of atoms appear in an intermediate position as IV, V, VI and VII respectively.

4. Dynamical theory: First approximation

The normal modes of atomic vibration in a crystal remain unaltered when a unit translation is given to the structure along any one of its three axes. Accordingly, it is sufficient to write down and solve the equations of motion of the atoms contained in any one unit cell of the structure. The features of the vibration deduced therefrom would equally well describe the possible atomic movements in the other cells of the structure. In the present problem, therefore, we have only to frame the equations of motion of a magnesium atom and of an adjoining oxygen atom in the structure for each of the possible modes of vibration deduced from the geometry of the structure. Their solution would give us the frequencies of those modes of vibration.

The forces acting on an atom which determine its movements are those arising from the displacements of other atoms in the crystal by reason of their mutual interactions. We shall proceed on the assumption that the interactions between any two atoms are determined by their *relative* displacements measured from the positions they occupy when at rest in the crystal. The forces of interaction may be expected to be greatest between atoms which are near neighbours and to diminish rapidly in respect of those atoms which are further and further removed from each other.

The nearest neighbours of each magnesium atom in the MgO structure are six oxygen atoms. These are situated in pairs, one on either side along the x , y and z axes of the structure. Likewise, each oxygen atom has six magnesium atoms as its nearest neighbours arranged in a similar fashion. We shall, in the first instance, proceed to work out the dynamics of the vibrations taking into account only the interactions between each magnesium atom and its six neighbouring oxygen atoms and vice versa. It is clear that two force-constants which we shall denote as α and β respectively would suffice to specify these interactions. The constant α refers to the interaction between an Mg atom and an O atom arising from their relative displacement *along* the direction of the cubic axis on which

they both lie. The force resulting from such displacement would be parallel to the direction of the displacement. The constant β refers to the interaction arising from a relative displacement *transverse* to the line joining the two atoms and parallel to one of the other two cubic axes. In this case as well, the resulting force would be parallel to the direction of such displacement.

We denote by m_1 and m_2 the masses of the Mg and O atoms respectively. ξ_1, η_1, ζ_1 and ξ_2, η_2, ζ_2 are the displacements of the Mg and O atoms under consideration respectively along the x, y and z axes. The forces acting on these atoms are found by multiplying the displacements of the interacting atoms relatively to each of them by the appropriate force-constants and adding them up. The equations are then solved by writing

$$\xi_1 = x_1 \sin \omega t, \quad \eta_1 = y_1 \sin \omega t, \quad \text{etc.},$$

and eliminating the quantities x_1, y_1 , etc., which represent amplitudes. An expression is then obtained which gives ω^2 in terms of α, β and the masses m_1 and m_2 . We shall consider in turn the different modes of vibration indicated by table 1 as possible for a face-centred cubic lattice.

The first case we shall consider is that in which the Mg atoms and O atoms oscillate as groups along the x -axis. The equations of motion are then

$$m_1 \frac{d^2 \xi_1}{dt^2} = -K_0(\xi_1 - \xi_2)$$

and

$$m_2 \frac{d^2 \xi_2}{dt^2} = -K_0(\xi_2 - \xi_1),$$

where K_0 is an abbreviation for $(2\alpha + 4\beta)$. Proceeding as already indicated, we obtain a quadratic equation for ω_1^2 , the solutions of which are

$$\omega_1^2 = \frac{K_0}{\mu}, \quad \omega_{10}^2 = 0, \quad (1)$$

where μ is the reduced mass given by the formula $1/\mu = 1/m_1 + 1/m_2$. The first solution represents mode I in table 2 above, while the zero frequency represents the translations appearing at the foot of that table.

The next case is that of the tangential oscillation of the cubic layers of atoms which are parallel to the yz plane along the y -axis. The alternate layers oscillate in opposite phases. The equations of motion are:

$$m_1 \frac{d^2 \eta_1}{dt^2} = -K_0 \eta_1 + 2\alpha \eta_2$$

and

$$m_2 \frac{d^2 \eta_2}{dt^2} = 2\alpha \eta_1 - K_0 \eta_2.$$

The solutions of these equations are:

$$\omega_{2,9}^2 = \frac{\frac{1}{2}K_0}{\mu} \pm \left[\frac{K_0^2}{4\mu^2} - \frac{(K_0^2 - 4\alpha^2)}{m_1m_2} \right]^{1/2}. \quad (2)$$

The alternative signs appearing in formula (2) give the frequencies of vibration ω_2 and ω_9 respectively. The higher frequency ω_2 refers to the case in which the Mg and O atoms appearing in the same yz planes move in opposite phases. The lower frequency ω_9 represents the case in which the Mg and O atoms appearing in the same yz planes move in the same phase. ω_2 and ω_9 refer respectively to the modes listed as II and IX in table 2. From formula (2) it is evident that

$$\omega_9^2 = \omega_1^2 - \omega_2^2.$$

The third case we shall consider is that in which the cubic layers of atoms in the crystal lying in the yz planes oscillate normally to themselves along the x -axis, the alternate layers being in opposite phases. The equations of motion are:

$$m_1 \frac{d^2\xi_1}{dt^2} = -K_0\xi_1 - (K_0 - 8\beta)\xi_2$$

and

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K_0 - 8\beta)\xi_1 - K_0\xi_2.$$

The solutions of these equations are:

$$\omega_{3,8}^2 = \frac{\frac{1}{2}K_0}{\mu} \pm \left[\frac{\frac{1}{4}K_0^2}{\mu^2} - \frac{32\alpha\beta}{m_1m_2} \right]^{1/2}. \quad (3)$$

The alternative signs appearing in the formula give the two frequencies of vibration ω_3 and ω_8 . The higher frequency ω_3 represents the case in which the Mg and O atoms which appear in any yz plane oscillate in the same phase, while the Mg and O atoms adjacent to each other in adjoining yz layers vibrate in opposite phases. The lower frequency ω_8 refers to the case in which the Mg and O atoms which appear in the same yz planes move in opposite phases, while the Mg and O atoms which are nearest to each other in adjacent yz layers oscillate in the same phase. ω_3 and ω_8 refer respectively to the modes listed as III and VIII respectively in table 2. From the formula (3), it is evident that

$$\omega_8^2 = \omega_1^2 - \omega_3^2.$$

We have next to consider the oscillations of the octahedral layers of atoms normally or tangentially to themselves. The Mg and O atoms are located in separate octahedral layers which alternate and are equidistant from each other. Hence, when two layers of Mg atoms oscillate in opposite phases, the layer of oxygen atoms midway between them remains at rest, and vice versa. A single equation of motion determines the frequency of oscillation for the magnesium atoms, while another such equation yields the frequency for the oxygen atoms. It

is also evident that when the interactions only with the nearest neighbours are considered, the frequency for oscillations normal and tangential to the octahedral planes would not be different. We obtain

$$\omega_{4,5}^2 = \frac{K_0}{m_2}, \quad (4)$$

for the modes listed as IV and V in table 2 and

$$\omega_{6,7}^2 = \frac{K_0}{m_1}, \quad (5)$$

for the modes listed as VI and VII in table 2.

5. Dynamical theory: Second approximation

In the foregoing, we took into account only the interactions between the atoms which are nearest to each other. This enables a first approximation to be obtained in a simple manner for the frequencies of vibration and permits of their being arranged, at least provisionally, in an ordered sequence. There is no difficulty, however, in taking the interactions with more distant neighbours into account and finding more exact formulae. Besides the six neighbouring oxygen atoms, each magnesium atom has twelve magnesium atoms as next nearest neighbours located on the face-diagonals. It has also eight oxygen atoms as more distant neighbours located on the body-diagonals. Likewise, each oxygen atom has twelve oxygen atoms as next nearest neighbours and eight magnesium atoms as more distant neighbours. The movements of these neighbours relatively to the atom under consideration and the interactions arising therefrom have to be taken into consideration in framing its equations of motion and deducing therefrom the frequencies of its vibration. We shall consider in succession the various modes of vibration listed in table 2.

Mode I.—In addition to the force-constants α and β already introduced, we have to consider a third force-constant γ , which expresses the interactions between the magnesium atoms and the oxygen atoms located along the body-diagonals of the cubic structure. It is readily shown that the frequencies are given by

$$\omega_1^2 = \frac{K}{\mu} \quad \text{or} \quad \omega_{10} = 0, \quad (6)$$

where K is an abbreviation for $(2\alpha + 4\beta + 8\gamma)$.

Modes II and IX.—In these modes, we have now to consider also the interactions of each Mg atom with the twelve Mg atoms in its neighbourhood.

Likewise, we have to take into account the interaction of each O atom with its twelve neighbouring O atoms. The forces and displacements with which we are concerned in these interactions are parallel to each other and to one or another of the three cubic axes. Four of the atoms are located in each of the three cubic planes containing the atom under consideration. It emerges that in four cases out of the twelve, the force and the displacement are both perpendicular to the cubic plane in which the interacting atoms are situated, while in the remaining eight cases, they are both parallel to that plane. We have accordingly to introduce two new force-constants θ_1 and ϕ_1 for the interactions between the magnesium atoms, and likewise two other force-constants θ_2 and ϕ_2 for the interactions between the oxygen atoms. The equations of motion then take the form

$$m_1 \frac{d^2 \eta_1}{dt^2} = - (K + 8\theta_1 + 8\phi_1)\eta_1 + (K - 4\beta - 16\gamma)\eta_2$$

and

$$m_2 \frac{d^2 \eta_2}{dt^2} = (K - 4\beta - 16\gamma)\eta_1 - (K + 8\theta_2 + 8\phi_2)\eta_2.$$

Substituting

$$\eta_1 = y_1 \sin \omega t \quad \text{and} \quad \eta_2 = y_2 \sin \omega t$$

and eliminating y_1 and y_2 , we obtain a quadratic equation which enables $\omega_{2,9}^2$ to be expressed in terms of the force-constants and the masses m_1 and m_2 .

Modes III and VIII.—Only five out of the seven force-constants already introduced appear in the equations of these two modes.

$$m_1 \frac{d^2 \xi_1}{dt^2} = - (K + 16\phi_1)\xi_1 - (K - 8\beta)\xi_2$$

$$m_2 \frac{d^2 \xi_2}{dt^2} = - (K - 8\beta)\xi_1 - (K + 16\phi_2)\xi_2.$$

Substituting

$$\xi_1 = x_1 \sin \omega t \quad \text{and} \quad \xi_2 = x_2 \sin \omega t,$$

and eliminating x_1 and x_2 , we obtain a quadratic equation which gives $\omega_{3,8}^2$ in terms of the force-constants and the masses m_1 and m_2 .

Modes IV, V, VI and VII.—We have now to introduce two additional force-constants ψ_1 and ψ_2 , which represent interactions in which the force and the displacement are mutually perpendicular, the displacement being along one cubic axis and the force along another cubic axis, while the interacting atoms lie in the plane defined by the two axes. ψ_1 refers to the case in which the interacting

atoms are both of magnesium, while ψ_2 refers to the case in which they are both oxygen atoms. These force-constants appear in considering the movements of the octahedral layers either normally or tangentially to themselves, by reason of the simultaneous movements along all the three cubic axes or along two cubic axes which need to be taken into account in these cases. The equations of motion for normal and tangential movements of a magnesium atom respectively are:

$$m_1 \frac{d^2 \xi_1}{dt^2} = - (K + 4\theta_1 + 8\phi_1 + 8\psi_1) \xi_1$$

and

$$m_1 \frac{d^2 \xi_1}{dt^2} = - (K + 4\theta_1 + 8\phi_1 - 4\psi_1) \xi_1.$$

The frequencies are therefore respectively:

$$\omega_6^2 = \frac{(K + 4\theta_1 + 8\phi_1 + 8\psi_1)}{m_1}$$

and

$$\omega_7^2 = \frac{(K + 4\theta_1 + 8\phi_1 - 4\psi_1)}{m_1}. \quad (7)$$

The equations of motion for normal and tangential oscillations of an oxygen atom are respectively

$$m_2 \frac{d^2 \xi_2}{dt^2} = - (K + 4\theta_2 + 8\phi_2 + 8\psi_2) \xi_2$$

and

$$m_2 \frac{d^2 \xi_2}{dt^2} = - (K + 4\theta_2 + 8\phi_2 - 4\psi_2) \xi_2.$$

The frequencies are therefore respectively

$$\omega_4^2 = \frac{(K + 4\theta_2 + 8\phi_2 + 8\psi_2)}{m_2}$$

and

$$\omega_5^2 = \frac{(K + 4\theta_2 + 8\phi_2 - 4\psi_2)}{m_2}. \quad (8)$$

6. Summary

The fundamental property of a normal vibration indicated by the classical dynamics, viz., that the particles in the system oscillate with the same frequency and in the same or opposite phases, considered in relation to the three-

dimensionally periodic structure of a crystal, enables the possible modes of atomic vibration in a crystal to be uniquely characterised and enumerated. The simplicity and high symmetry of the structure of MgO enables this procedure to be carried further and the modes of normal vibration to be completely described and explicit formulae obtained from their frequencies. It emerges that the structure of MgO has nine distinct frequencies of vibration. Expressions have been derived for these frequencies of these modes, both in the first and in the second approximation.

The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part III. Comparison of theory and experiment

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1. Introduction

Part I of this memoir dealt with the observed infra-red behaviour of MgO over the spectral range covered by the instruments at the disposal of the author. In part II, the normal modes of vibration of the atomic nuclei in the crystal about their positions of equilibrium were deduced from the principles of classical mechanics and expressions were given for the frequencies of the nine modes which were shown to be possible. In the present part, we shall concern ourselves with a comparison of the results of experiment and the consequences of the theory. Such a comparison has necessarily to be based on the nature of the relationship between infra-red activity and the modes of vibration of the atomic nuclei. We shall freely make use of the ideas and principles which have emerged from studies on the infra-red behaviour of diatomic, triatomic and polyatomic molecules, as also of crystals having more complex structures. It will be found that these ideas and principles when applied to the particular circumstances of the case enable a highly satisfactory concordance to be established between the facts of experiment recorded in part I of the memoir and the dynamical theory developed in part II.

2. Infra-red activity of the first order

A fact which emerges very clearly from the experimental studies described in part I is that the normal mode which is strongly active as a fundamental has also the highest frequency of all the active normal modes. The theoretical formulae for the frequencies obtained and set out in part II also show that the mode of vibration in which the Mg and the O atoms oscillate in opposite phases and in which the oscillation repeats itself from cell to cell without change of phase has a higher frequency than all the other eight modes. This is obvious from the approximate formulae given in section 4 of part II and the situation is not altered when the

higher approximations set out in section 5 are considered. It is further evident that this normal mode would exhibit a powerful infra-red activity of the first-order. For, the displacements of electric charge resulting from the approach to or recession from each other of the two dissimilar atoms Mg and O would occur in the same phase in the successive cells of the structure and hence their effects would be cumulative.

Considering now the eight other normal modes, they can all be described as movements of the Mg atoms or of the O atoms alone or of both sets of atoms together in one or another of the different directions permitted by the symmetry of the structure. But a common feature of all the eight modes is that these movements alternate in phase along one or two or all three of the directions which are the edges of the unit rhombohedral cell of the lattice. Hence, the displacements of charge in the successive cells of the structure are in alternate phases. Therefore, when summed up over an element of volume including a block of eight contiguous cells in the structure, the displacements of charge would cancel out. It follows that all the eight modes under reference would fail to exhibit any infra-red activity of the first-order. In other words, we cannot expect their fundamental frequencies to manifest themselves as absorption maxima in the spectrographic records. This again is in agreement with what is actually observed.

Here a distinction must be drawn between the four normal modes which involve simultaneous movements of the Mg and O atoms in directions which are either normal or tangential to the cubic planes of the crystal and the four other normal modes in which the Mg atoms alone or the O atoms alone oscillate in directions which are normal or tangential to the octahedral planes of the crystal. As has already been remarked in part II, the Mg atoms and the O atoms appear in distinct layers in the octahedral planes in such manner that each Mg layer has O layers on either side of it at the same distance and each O layer has likewise Mg layers situated symmetrically on either side. Further, in the normal modes of these four species, the Mg layers on either side of the O layers, or the O layers on either side of the Mg layer oscillate in opposite phases. As a consequence, the displacements of electric charge on either side of the middle layer are in opposite directions. When summed up over the volume element containing eight unit cells of the structure, they cancel out. Such cancellation is clearly *absolute*; in other words, it is not limited to the case in which the movements of charge are regarded as of very small amplitude and therefore strictly harmonic in character.

Thus, the two categories of normal modes, viz., those in which the Mg and O atoms oscillate simultaneously and those in which they oscillate separately stand on a different footing. The former are inactive in the first-order absorption by reason of the alternation of phase in the successive cells of the structure. The absence of activity depends on the oscillation being of small amplitude and the displacements of charge resulting therefrom being of equal magnitude but opposite in phase in successive cells. On the other hand, in the second category, the cancellation is effective irrespective of the actual amplitude of the oscillations.

3. Infra-red activity of higher orders

The considerations set forth above naturally lead us to consider the possibility of the normal modes exhibiting infra-red activity of higher orders, in other words of manifesting themselves in the absorption spectra as overtones of the fundamentals. The appearance of overtones in the infra-red absorption spectra of diatomic and polyatomic molecules is a familiar fact of experience. It is also well known that they are much weaker than the fundamentals, which is indicated by the fact that their observation needs the use of much thicker absorbing layers. The explanation usually given for their appearance is based on the hypothesis of the anharmonicity of the molecular vibrations of which the effect comes into prominence when the oscillations of the atomic nuclei are of very large amplitude. In these circumstances, the periodic displacements of electric charge which give rise to the absorption of infra-red radiation include components not only of the fundamental frequencies but also the overtones of those frequencies. Absorption of the energy of radiations having the overtone frequencies and its transformation to the energy of nuclear vibrations is thereby made possible.

The important point regarding the infra-red activity of higher orders is that the amplitudes of nuclear vibration should be large. Even when this condition is satisfied, considerations regarding the symmetry of the modes of vibration may, in particular cases, totally exclude the manifestation of the effect of the periodic displacements of charge and hence also the possibility of the infra-red activity of all orders. We have already noticed such a situation in the case of the modes involving oscillation of the Mg atoms alone or of the O atoms alone in directions normal or tangential to the octahedral layers. Hence these four modes could not be expected to manifest themselves as overtones in the infra-red absorption spectra. The position is different in regard to the five other modes which involve simultaneous movements of the Mg and the O atoms. No such restriction based on considerations of the symmetry appears in their cases. Hence we may expect overtones of all these five modes to manifest themselves in the absorption spectra, provided the necessary condition of the largeness of the amplitudes of the nuclear vibrations is satisfied.

The dynamical theory set out in part II of the memoir is based on the well known theorem in classical mechanics regarding the small vibrations of a connected system of particles about their positions of equilibrium. The theorem enables the relative magnitudes of the amplitudes of their vibration in any particular normal mode to be evaluated. But it leaves their absolute magnitudes undetermined. But, since we are now concerned with the absorption of radiation, the introduction of the ideas of the quantum theory, which is inevitable, results in making the amplitudes of vibration fully determinate. The incident radiation consists of energy quanta of magnitude $h\nu$. Assuming for the sake of simplicity that the oscillators are strictly harmonic with a frequency ν_0 , their energy would go up with increasing amplitude by successive equal steps of

$h\nu_0$. The successive orders of absorption would then appear as a consequence of equating $h\nu$ to $h\nu_0$, or $2h\nu_0$ or $3h\nu_0$ or $4h\nu_0$. Mechanical anharmonicity of the oscillators would only result in the energy values deviating from this regular harmonic sequence. What is needed for the possibility of infra-red activity of higher orders is that the oscillations of electric charge associated with the nuclear movements should include a harmonic series of components having the frequencies $2\nu_0, 3\nu_0, 4\nu_0$, etc. The energy of radiation having those frequencies can then be taken up by the moving charges and transferred to the atomic nuclei as energy of mechanical movement, in other words, as heat energy.

From what has been stated, it is clear that if we identify the mechanical oscillators in the crystal as *domains of macroscopic size*, infra-red absorptions of orders higher than the first would be impossible. For, when the oscillatory energy of such a domain is quantised, the actual amplitudes of oscillation of the atomic nuclei and therefore also the movements of electric charge associated with them would be infinitesimal. The only possibility would then be the absorption of the first-order in which $h\nu = h\nu_0$ and absorptions of higher order cannot arise. Thus, for absorptions of higher order to be at all possible, we must assume the oscillators in the crystal to be of extremely small dimensions, in other words to be the unit cells of the crystal structure or small groups of such unit cells. The oscillators whose normal modes were listed and enumerated in part II of the memoir were twice as large in each direction as the unit cells of the crystal structure. If their energies are quantised, the amplitude of the atomic oscillations in domains of such small size would be sufficiently large to permit of infra-red absorption of higher orders than the first.

We may sum up the results of this discussion by the statement that of the nine normal modes listed in table 2 of part II of the memoir, mode I would be active both as a fundamental and as overtones, modes II, III, VIII and IX would be inactive as fundamentals but could be active as overtones, while modes IV, V, VI and VII would not be active either as fundamentals or as overtones.

4. Frequencies of the active modes

The frequencies of the normal modes of vibration were derived in section 4 of part II on the assumption that the only interactions which need be taken into account are those between unlike atoms in the structure. This assumption is valid only in respect of the active mode of the highest frequency. The approximate formulae derived on that basis are however useful as they enable the frequencies of the five active modes to be expressed in terms of each other. Two force-constants appear in the formulae, viz., α and β , α being the longitudinal and β the transverse component of the interaction between adjacent unlike atoms. It may be presumed that α is greater than β , but the ratio of α to β is not known. We

Table 1. Frequencies of the normal modes: Observed and calculated (cm^{-1})

	Mode I	Mode II	Mode III	Mode VIII	Mode IX
Observed	490	423	365	313	277
Calculated	490	428	380	309	237
$\alpha = 2\beta$					
Calculated	490	441	393	293	212
$\alpha = 3\beta$					
Calculated	490	408	408	271	270
$\alpha = \beta$					

assume the highest frequency of the five to be 490 cm^{-1} and compute the others for various values of the ratio α/β , viz., $\alpha = \beta$, $\alpha = 2\beta$ and $\alpha = 3\beta$. Table 1 above shows the results thus obtained.

It will be seen that the five frequencies follow each other in the same order for all three α/β ratios, though the actual magnitudes of the calculated frequencies are different. The best agreement between the calculated and the spectroscopically determined frequencies results from the most reasonable assumption for the α/β ratio, viz., that $\alpha = 2\beta$. The mode of lowest frequency, viz., mode IX, is however seen to be an exception. Mode IX, it may be remarked here, is an oscillation of the cubic planes tangential to themselves, the Mg and the O atoms in those planes moving in the same phase. Like all the other modes listed in table 1 except the first, it is inactive as a fundamental but active as an octave. By the nature of the case, however, such activity would be feeble. Referring to the absorption curves of the thinnest MgO film reproduced as the upper of the two records in figure 10 of part I of this memoir, it will be noticed that the transmission falls off more steeply in the region of wavelengths greater than 20μ than towards shorter wavelengths. The form of the graph between 16μ and 20μ indicates that a specific absorption is operative which is located midway between them, viz., at about 18μ . We are, therefore, justified in adding 277 cm^{-1} and the wavelength 36μ to the list of normal modes and their characteristic wavelengths in the summary of experimental results which concludes part I.

5. Relation between reflectivity and infra-red absorption

We may now proceed to discuss the manner in which the reflecting power of the surface of an MgO crystal changes with wavelength in the spectral range between 13μ and 36μ . The experimental results obtained and reported by Burstein,

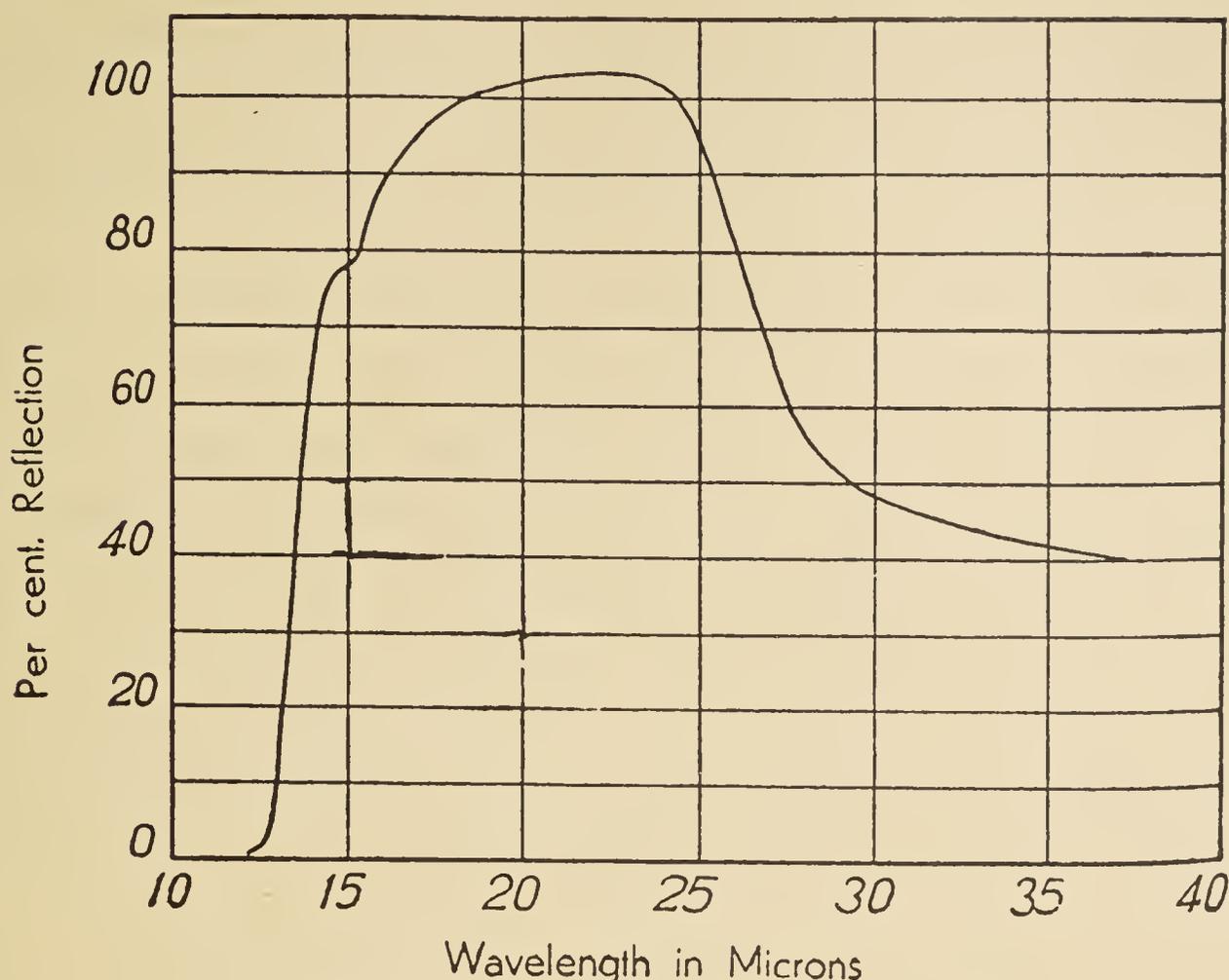


Figure 1. Reflecting power of MgO surface.

Oberly and Plyler (1948) have already been referred to in part I of this memoir. Their figure which shows the reflecting power as compared with an aluminium mirror is reproduced as figure 1 above in the text. One might expect that the peak of the reflecting power would appear at the wavelength 20.4μ which corresponds to the active fundamental frequency of 490 cm^{-1} . However, we have also to consider in this connection, the other normal modes of vibration of the crystal. Besides the active fundamental at 20.4μ , there is the inactive fundamental close to it in frequency which has a characteristic wavelength at 23.64μ and a series of other inactive fundamentals at still greater wavelengths, viz., 27.4μ , 32μ and 36μ . Then again, in the region of wavelengths less than 20.4μ , octaves of the normal modes appear which have their characteristic wavelengths at 10.2μ , 11.82μ , 13.7μ , 16μ and 18μ respectively. All these octaves have been shown to be active in absorption. The possibility therefore arises of their making an observable contribution to the reflecting power of an MgO surface.

As already noticed, the absorptions located at 10.2μ and 11.82μ are so weak that they can only be recorded with comparatively thick plates. We may, therefore, exclude them from consideration and need only take note of the absorptions located at 13.7μ , 16μ and 18μ . It is significant that the reflective power of MgO reaches large values in this range of wavelengths. It rises very steeply at about 13.7μ and after exhibiting an inflexion or arrest at 15μ , goes up

again in the wavelength range between $16\ \mu$ and $18\ \mu$ before it reaches the peak reflectivity beyond $20\ \mu$. Indeed, the course of the reflectivity curve is itself the clearest demonstration that the octaves at $13.7\ \mu$, $16\ \mu$ and $18\ \mu$ contribute notably to the reflecting power; the arrest at $15\ \mu$ arises from the frequency gap between the first two.

Figure 1 shows that the reflecting power continues to increase a little beyond $20.4\ \mu$ and is greatest at about $24\ \mu$. Beyond $24\ \mu$, it falls rather quickly at first and then more slowly, but remains large up to $35\ \mu$ and beyond. These facts find a natural explanation if we assume that the second fundamental having its characteristic wavelength at $23.64\ \mu$ makes a notable contribution to the reflecting power. This is indeed to be expected. For, when the frequency of the radiation is equal to or near the frequency of the active fundamental, the movements of electric charge at and near the surface of the crystal would be large. In these circumstances, the different normal modes of vibration may be expected to influence each other in such a manner that a mode which is ordinarily inactive could be excited to activity. That the observed powerful reflection extends up to $24\ \mu$ and even beyond it is therefore not surprising.

6. Frequencies of the inactive modes

The approximate formulae given in section 4 of part II enable us also to evaluate the frequencies of the inactive modes, viz., those in which the O atoms alone or the Mg atoms alone oscillate in terms of the highest active frequency, viz., $490\ \text{cm}^{-1}$. We obtain $380\ \text{cm}^{-1}$ and $309\ \text{cm}^{-1}$ respectively as the frequencies of vibration of the O and of the Mg atoms. It is evident, however, that these figures are an underestimate of the actual frequencies of these modes. For, as is also clear from the formulae of section 5 of part II, the frequencies of these modes are determined by the interaction of each oscillating atom with the six like atoms in its immediate vicinity as well as with the six unlike atoms which are its nearest neighbours. As the distance between like atoms is only $\sqrt{2}$ times the distance between unlike atoms, we may safely assume that the two sets of interactions would be of comparable magnitudes and hence that the vibration frequencies would be definitely greater than $380\ \text{cm}^{-1}$ and $309\ \text{cm}^{-1}$ indicated by the first approximation.

The neglect of the interactions between like atoms also results in the frequencies of oscillations of the Mg and of the O atoms normal to the octahedral planes having the same frequency as oscillations tangential to them. Actually, however, oscillations normal to the octahedral planes may be expected to have frequencies noticeably greater than the modes tangential to those planes.

Earlier, it was remarked that by reason of their geometric symmetry, modes IV, V, VI and VII would be totally inactive, in other words, that they would be wholly

inaccessible to observation by the methods of infra-red spectroscopy. This statement was, however, based on the assumption that the normal vibrations of the structure are completely independent of each other. Since, however, we are concerned with the infra-red activity of higher orders than the first, the amplitudes of vibrations involved are not small and the normal modes cannot therefore be completely independent of each other. The possibility thus arises of the inactive modes or rather of their overtones revealing themselves in the spectroscopic records by a species of induced activity resulting from the contiguity of their frequencies to the frequencies of strongly active modes.

Referring to the spectrographic records reproduced as figures 3, 4, 5, 6, 7 and 8 in part I of this memoir, it will be noticed that the transmission curve in the region between 10.2μ and 11.82μ exhibits certain curious features appearing in all of them and at precisely the same spectral wavelengths. The transmission which is a minimum at 10.2μ rises to a maximum and then drops to the second minimum at 11.82μ ; but between the two minima, the graph does not follow a smooth curve but bends inwards more or less sharply in the vicinity of two wavelengths, one on either side of the 11μ ordinate. One such bend may be located at 10.8μ and the other at 11.2μ . The sharp bends at these two positions appear very clearly, for example, in figure 6 of part I. The frequencies in wave-numbers at which these singularities appear are respectively 925 cm^{-1} and 893 cm^{-1} . If we assume that they represent the octaves of two normal modes exhibiting induced activity, their frequencies would be 463 cm^{-1} and 446 cm^{-1} , substantially greater than the 380 cm^{-1} indicated by the rough calculation in which the interactions between the oxygen atoms nearest to each other are totally ignored. But the increases are not greater than what might be expected to result from such interactions being taken into account.

The induced activity of modes VI and VII in which the magnesium atoms alone oscillate is not so conspicuously exhibited in the spectrograms reproduced in part I of this memoir. Indications of them, however, appear in the wavelength range between 12μ and 13μ in figures 6, 7 and 8 of part I. The sharp bends in the transmission curve at 12.5μ and at 12.9μ noticed in figure 8 are perhaps their clearest manifestation. Interpreting these singularities as arising from the octaves of the normal modes VI and VII, we obtain their characteristic wavelengths at 25μ and 25.8μ respectively and their characteristic frequencies as 400 cm^{-1} and 387 cm^{-1} . These are substantially higher than the rough value of 309 cm^{-1} which results when we neglect the interactions between each magnesium atom and the six nearest magnesium atoms which appear in the more exact expressions for the frequencies of these modes. The observed frequencies indicate that these interactions are far from being weak or negligible. The electron atmospheres of the magnesium atoms extend further from their nuclei and hence would come into closer contact with each other in the unit cells of the structure than would be the case for the oxygen atoms. Hence the forces of interaction as between like atoms may be expected to be even more powerful for Mg than for O atoms.

7. Some concluding remarks

Our purpose so far has been to show how closely the consequences of the dynamical theory set out in part II and the observed infra-red behaviour of MgO in absorption and in reflection described in part I fit into each other and how we are thereby enabled to obtain a clear and comprehensive view of the subject. Formal considerations based on the concept of interatomic forces, of displacements of electric charge resulting from atomic movements and of their symmetry characters were sufficient for that purpose. It would not, however, be superfluous to add a few remarks here regarding other fundamental aspects of the infra-red behaviour of crystals.

A question of some importance is the role played respectively by the atomic nuclei and by the electrons in the infra-red activity of crystals. The displacements of the massive atomic nuclei from their positions of equilibrium are necessarily involved, since the frequency of the absorbed radiation is identical with or approximates to a frequency of vibration of the atomic nuclei about their positions of equilibrium or to a small multiple thereof. But we have also to emphasise the part played by the electrons which hold the nuclei together and determine the magnitude of the interatomic forces and hence also effectively determine the frequencies of the nuclear vibrations. There can be little doubt that it is the displacement of these electrons induced by the field of the incident radiation which is the effective cause of infra-red absorption. The nuclear movements can make no direct contribution of importance to the displacements of electric charge. For, the oscillations of some of the atomic nuclei are in opposition of phase to the oscillations of the others and hence their effects would cancel out.

It follows from what has been stated above that the dynamic theory of the vibrations of the atomic nuclei and its consequences represent only one aspect of the subject of the infra-red behaviour of crystals. The other aspect is the behaviour of the electrons which hold the nuclei together in their places. These two aspects are closely related to each other. Hence, while there should be an easily observable correlation between the features of the vibration spectra of the atomic nuclei deduced from the theory and the spectral characters of the absorption and reflection of infra-red radiation as found in experiment, a complete agreement in respect of all details of their features is scarcely to be expected.

8. Summary

The description of the nine normal modes of vibration and their frequency formulae given in part II enable them to be grouped together in respect of infra-red activity and arranged in each group in diminishing order of frequency. A

detailed comparison then becomes possible between the consequences of the theory and the experimental results set out in part I. A comprehensive and satisfactory agreement emerges from the comparison. The modes can be identified and their frequencies determined directly from the spectroscopic records. The manner in which the reflectivity of an MgO surface varies with the wavelength of the infra-red radiation also receives a satisfactory elucidation.

The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part IV. Evaluation of its specific heat

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1. Introduction

Einstein's classic paper of 1907 introducing his theory of specific heats was based on an application of the fundamental notions of the quantum theory and of thermodynamics to the problem of determining the thermal behaviour of a body assumed to be constituted of a great number of structural elements, each of which is an oscillator having a definite frequency of vibration. Basing himself on the assumption that their energy of vibration obeys the quantum rules, Einstein obtained an expression for the total vibrational energy of the body, in other words for its heat content, in terms of the frequency or frequencies of vibration of the oscillators, their numbers and the absolute temperature. Einstein's theory and its results may be summed up by the statement that the thermal energy content of a substance is determined by the vibration spectrum of the elementary structures of which it is constituted.

A well known theorem in classical mechanics states that the small vibrations of a system of particles result from the superposition of a set of normal modes, in each of which the particles of the system vibrate with the same frequency and in the same or opposite phases, the total number of normal modes being the same as the number of degrees of dynamic freedom of the system. The normal modes in the sense of this theorem which the structure of a crystal can exhibit may be readily deduced. The argument is the same as that used earlier in part II of this memoir for the particular case of the MgO structure. If each unit cell of the crystal contains p atoms, the crystal has $(24p - 3)$ species of normal modes; this number is the same as the degrees of dynamic freedom of the group of $8p$ atoms included in a volume element of which the dimensions are twice as large as those of the unit cell; the three omitted modes are the translatory movements of the group.

In the earlier parts of this memoir it has been shown that the 45 species of normal modes indicated by the general theory for MgO ($p = 2$) reduce to nine only by reason of the cubic symmetry of the crystal. These nine modes were

Table 1. Normal modes and frequencies

Description of the mode	Degeneracy	Frequency in cm^{-1}
Oscillation of the Mg and O atoms in the unit cells in opposite phases	3	490 obs.
Normal oscillation of the O atoms in the octahedral planes	4	463 obs.
Tangential oscillation of the O atoms in the octahedral planes	8	446 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in opposite phases	6	423 obs.
Normal oscillation of the Mg atoms in the octahedral planes	4	400 obs.
Tangential oscillation of the Mg atoms in the octahedral planes	8	387 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in the same phase	3	365 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in opposite phases	3	313 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in the same phase	6	277 obs.
Continuous spectrum	3	277 \rightarrow 0

described and their activity in the absorption and reflection of infra-red radiation was discussed. It emerged that the theory accounts in a highly satisfactory and comprehensive fashion for the observed spectroscopic properties of MgO.

We shall now proceed to show that the thermal energy content of the MgO crystal and its variation with temperature can be fully worked out on the basis of the same theory as its spectroscopic behaviour. We shall make use of the original ideas of Einstein and the spectroscopic data derived from our experimental studies. The specific heat of MgO and its variation with temperature thus deduced are found to be in complete agreement with the experimental data reported in the literature. It is significant that no use whatever is made of data regarding any other properties of MgO in this connection. The power and validity of the present approach to specific heat theory are thus demonstrated.

2. The vibrational spectrum of MgO

Table 1 given above is self-explanatory. It assembles the relevant particulars set out and discussed in the preceding parts of the memoir. The total of the degeneracies listed in the second column of the table is 48, which is also the number of degrees of dynamic freedom of a group of 8 O atoms and 8 Mg atoms which forms the dynamic unit in the crystal structure. The number of such groups

is one-eighth of the number of MgO "molecules" present in the crystal. This 16-atom group is the oscillator with which we are concerned in specific heat theory. Forty-five out of its 48 degrees of freedom are manifested as the discrete frequencies listed in the third column of the table. The remaining three degrees of freedom are the translations of the oscillator. They appear as the last entry of the table and are there described as a continuous spectrum with a degeneracy 3 and ranging in frequency from 277 cm^{-1} down to zero. The justification for these entries will appear later.

To determine the contributions to the molecular heat of the modes with discrete frequencies shown in the third column of table 1 we use the available tabulations of the Einstein specific heat function and find its value for the particular frequency at the particular temperature under consideration. *Twice the value of the Einstein function multiplied by the degeneracy of the mode and divided by 48 gives the contribution of the mode to the molecular heat of MgO.* Proceeding in this fashion for all the nine frequencies we can sum up the results obtained. Dividing the total obtained by 40.32 which is the molecular weight of MgO, we obtain a tabulation of the specific heat of MgO as a function of the temperature, in so far as it arises from the spectrum of vibrations with discrete frequencies.

In the general case of a crystal containing p atoms in each unit cell, the $(24p - 3)$ normal modes of vibration account for all the degrees of freedom of movement of the group of $8p$ atoms which is the oscillator in specific heat theory except for the three degrees which represent its translations. Even in the case of the crystals with the simplest structure ($p = 1$) these translations take up only three out of every 24 degrees of freedom. When $p = 2$, as in the case of MgO, the translations represent only three out of 48 degrees of freedom. In the case of more complex crystals they form an even smaller proportion of the whole. Nevertheless, the movements within the crystal which they represent and the contributions which these make to the thermal energy cannot be ignored. We shall now proceed to consider these matters.

3. The residual spectrum

The translations of an atomic group within a crystal would necessarily tend to displace neighbouring atomic groups and hence would set up forces resisting the movement. We are therefore led to conclude that the degrees of freedom which do not appear as internal vibrations of our dynamic units would manifest themselves as internal vibrations in elementary volumes of larger dimensions. The larger such an element of volume is, the lower would be the limit of its possible frequencies of vibration. Hence, the translations of our atomic groups would be associated with vibrational movements in the crystal whose frequencies extend from the upper limit set by the frequencies of their internal vibration down to very

low values. In other words, the vibration spectrum of MgO with its discrete set of frequencies would be supplemented by a residual spectrum which is continuous and extends down to zero frequency.

We have now to determine how the modes of vibration referred to above are distributed with respect to frequency in the residual spectrum. Low frequencies arise from internal vibrations in volume elements of large size. The number of such elements included within the crystal diminishes rapidly with increase of their linear dimensions. It follows that the density of the vibrational modes in the residual spectrum would fall off quickly as their frequency diminishes.

Consider two sets of volume elements whose linear dimensions are respectively m and n times greater than those of the atomic groups which we have recognised as the dynamic units of crystal structure. The number of such volume elements would be respectively $1/m^3$ and $1/n^3$ times smaller than the number N in the crystal of atomic groups referred to. Let ν_m and ν_n be respectively the lowest frequencies of internal vibration of these volume elements. We may reasonably assume that the vibration frequencies are inversely proportional to the linear dimensions of the oscillators. We may accordingly write $\nu_m = f/m$ and $\nu_n = f/n$, where f is a constant having the dimensions of a frequency. In the limit when m approaches n , we may write $\nu_m - \nu_n = d\nu$. The number of oscillators whose frequencies lie within the range $d\nu$ would be thrice the difference in the number of volume elements whose lowest frequencies are respectively ν_m and ν_n , and is thus the same as $3N(1/m^3 - 1/n^3)$ in the limit where m approaches n . We may write this difference as $9N\nu^2 d\nu/f^3$. Integrating it over the whole frequency range covered by the residual spectrum, we should regain the number $3N$. We are thereby enabled to identify the constant f with the upper frequency limit ν_L of the residual spectrum. The vibrational modes are thus distributed in the residual spectrum in the manner defined by the function $9N\nu^2 d\nu/\nu_L^3$.

Thus, to find the contribution to the thermal energy of the crystal arising from the residual spectrum of vibrations, we multiply the average energy of an oscillator of frequency ν as given by Einstein's theory by the number of such oscillators distributed over its range of frequency as deduced above and integrate the product between the limits ν_L and zero. The contribution to the specific heat would then be the differential of the energy thus evaluated with respect to temperature. The functions which come up for computation in this procedure are well known and as tabulations of them are available, it is a simple matter to find the contributions to the specific heat of MgO arising from the residual spectrum at various temperatures. These are then added to the contributions of the Einstein terms arising from the nine discrete frequencies of the lattice at the respective temperatures. The upper limit ν_L of the frequency range covered by the residual spectrum in this evaluation is necessarily the lowest of the nine discrete frequencies of MgO, viz., 277 cm^{-1} . The contribution of the residual spectrum to the specific heat at different temperatures evaluated in this manner has been entered in tables 2, 3 and 4 as the last entry 3D(277) after the contribution of the

Table 2. Computation of specific heat

	50° K	75° K	100° K	125° K	150° K	175° K	200° K	225° K
3E(490)	0.0001	0.0049	0.0300	0.0805	0.1465	0.2163	0.2824	0.3414
4E(463)	0.0002	0.0100	0.0529	0.1315	0.2281	0.3254	0.4144	0.4921
8E(446)	0.0007	0.0255	0.1258	0.2984	0.5016	0.7003	0.8789	1.0325
6E(423)	0.0010	0.0269	0.1189	0.2643	0.4258	0.5784	0.7114	0.8240
4E(400)	0.0011	0.0252	0.0993	0.2069	0.3202	0.4228	0.5105	0.5830
8E(387)	0.0031	0.0605	0.2253	0.4525	0.6841	0.8900	1.0629	1.2049
3E(365)	0.0020	0.0310	0.1038	0.1965	0.2858	0.3625	0.4255	0.4764
3E(313)	0.0067	0.0629	0.1649	0.2715	0.3624	0.4347	0.4909	0.5342
6E(277)	0.0302	0.1993	0.4432	0.6653	0.8405	0.9729	1.0717	1.1463
3D(277)	0.1003	0.2420	0.3700	0.4647	0.5315	0.5787	0.6125	0.6372
Mol. heat	0.1454	0.6882	1.7341	3.0321	4.3265	5.4820	6.4611	7.2720
Sp. heat	0.0036	0.0171	0.0430	0.0752	0.1073	0.1360	0.1602	0.1804

Table 3. Computation of specific heat

	250° K	275° K	300° K	350° K	400° K	450° K	500° K
3E(490)	0.3926	0.4364	0.4736	0.5321	0.5746	0.6059	0.6297
4E(463)	0.5586	0.6146	0.6616	0.7346	0.7870	0.8258	0.8547
8E(446)	1.1620	1.2708	1.3612	1.5007	1.6000	1.6731	1.7283
6E(423)	0.9178	0.9952	1.0591	1.1568	1.2259	1.2764	1.3122
4E(400)	0.6428	0.6913	0.7313	0.7916	0.8336	0.8648	0.8869
8E(387)	1.3205	1.4146	1.4906	1.6059	1.6867	1.7429	1.7892
3E(365)	0.5171	0.5500	0.5765	0.6163	0.6439	0.6627	0.6790
3E(313)	0.5680	0.5946	0.6161	0.6475	0.6690	0.6841	0.6949
6E(277)	1.2035	1.2481	1.2832	1.3340	1.3692	1.3929	1.4109
3D(277)	0.6558	0.6700	0.6811	0.6971	0.7079	0.7154	0.7208
Mol. heat	7.9387	8.4850	8.9343	9.6166	10.0978	10.4440	10.7066
Sp. heat	0.1969	0.2104	0.2216	0.2385	0.2504	0.2590	0.2655

discrete frequencies. The latter are determined from the respective Einstein functions and are indicated in these tables as 3E(490), 4E(463), etc.

4. Comparison with the measured specific heats

The specific heat of MgO has been the subject of experimental determination by several investigators over different ranges of temperature. Their data have been collected and put together in the form of a table at convenient intervals of

Table 4. Computation of specific heat

	550° K	600° K	650° K	700° K	750° K	800° K	850° K
3E(490)	0.6483	0.6615	0.6754	0.6835	0.6906	0.6969	0.7022
4E(463)	0.8757	0.8952	0.9088	0.9191	0.9282	0.9358	0.9423
8E(446)	1.7673	1.8054	1.8281	1.8482	1.8652	1.8799	1.8915
6E(423)	1.3440	1.3653	1.3821	1.3961	1.4079	1.4176	1.4255
4E(400)	0.9058	0.9180	0.9286	0.9371	0.9442	0.9500	0.9547
8E(387)	1.8210	1.8451	1.8649	1.8815	1.8943	1.9053	1.9141
3E(365)	0.6890	0.6975	0.7044	0.7097	0.7141	0.7176	0.7207
3E(313)	0.7033	0.7097	0.7144	0.7187	0.7221	0.7247	0.7269
6E(277)	1.4239	1.4340	1.4421	1.4486	1.4536	1.4581	1.4616
3D(277)	0.7247	0.7279	0.7303	0.7323	0.7338	0.7352	0.7362
Mol. heat	10.9030	11.0596	11.1791	11.2748	11.3540	11.4211	11.4757
Sp. heat	0.2704	0.2743	0.2773	0.2796	0.2816	0.2833	0.2846

Table 5. Measured specific heats of MgO

Absolute temperature	53°	73°	93°	123°	173°	223°
Specific heat	0.0033	0.0158	0.0358	0.0741	0.1290	0.1768
Absolute temperature	273°	323°	373°	473°	673°	873°
Specific heat	0.2078	0.2317	0.2437	0.2604	0.2771	0.2915

temperature in the *International Critical Tables* (Vol. V, 1929, page 98). They are reproduced in table 5 after conversion from joules to calories.

A comparison of the figures appearing in table 5 with the calculated specific heats at the nearest temperatures appearing in tables 2, 3 and 4 shows that the variation of specific heat with temperature as actually measured is well represented by the theoretical computations. The excellence of the agreement is made clearer in figure 1 where the theoretical curve is drawn as a continuous line while the dots represent the experimental data.

At the lowest temperature of 50° K listed in table 2, the contribution of the residual spectrum to the specific heat forms the largest part of the whole. But as the temperature rises, its relative importance diminishes rapidly, being only 1/5th of the whole at 100° K and 1/10th at 200° K. It thereafter diminishes progressively to its limiting value of 1/16th. These changes are a consequence of the continued increase with rising temperature of the contributions of the discrete frequencies to the specific heat, while on the other hand, the contribution of the residual spectrum soon reaches its limiting value. It will be noticed from tables 2 and 3 that E(277) and D(277) become nearly equal to each other at temperatures higher

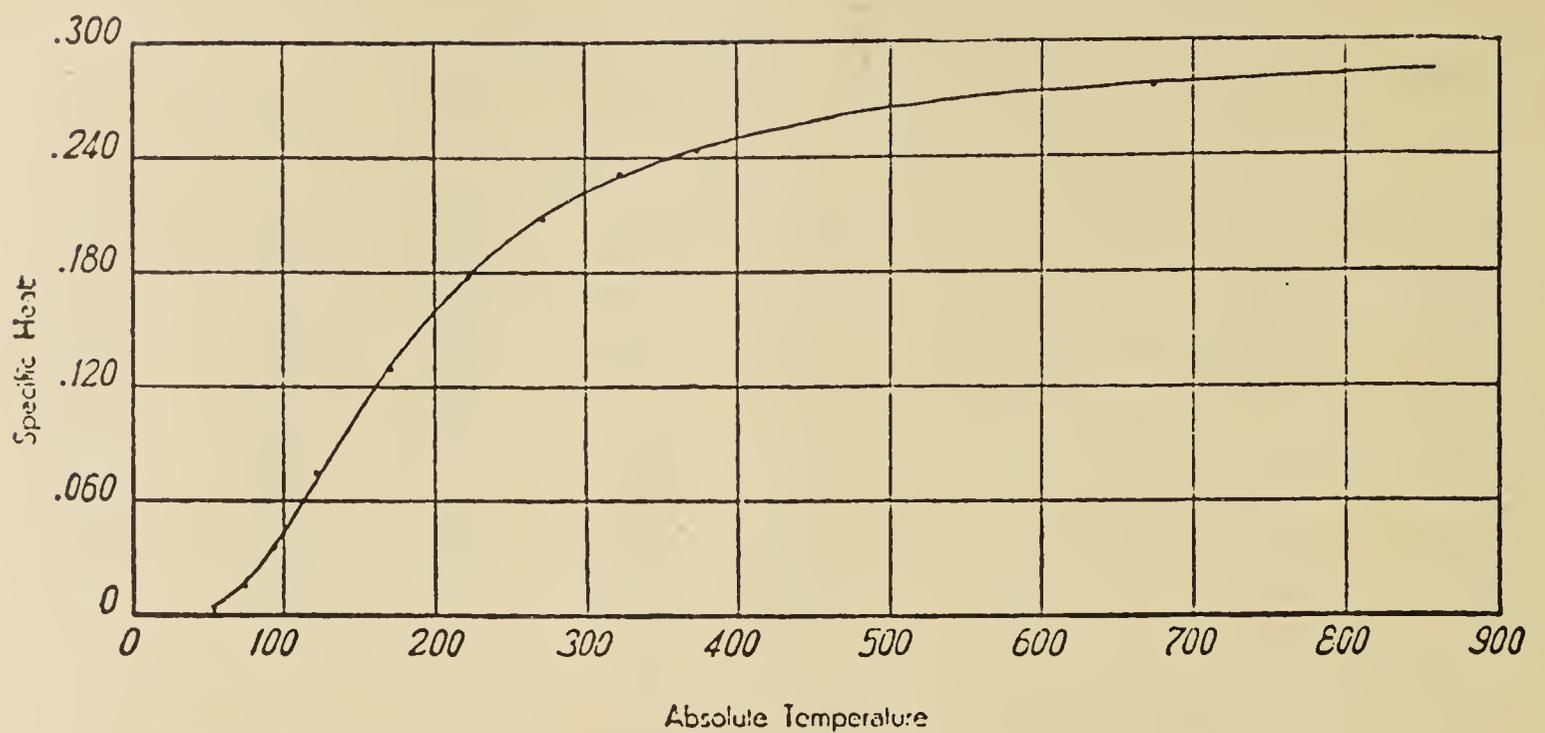


Figure 1. Specific heat of MgO. Calculated———. Observed ● ● ● ●.

than 250° absolute. This is a consequence of the fact that the vibrational modes appearing in the residual spectrum are clustered near its upper limit of frequency. This is equivalent to stating that the residual spectrum arises for the most part from internal oscillations in volume elements whose dimensions are not very much larger than those of the dynamic units in the crystal. A great majority of them may be about four times as large in each direction as the unit cells of the crystal structure. Only at the very lowest temperatures, when the modes of higher frequencies cease to be excited, would any appreciable part of the thermal energy be ascribable to oscillators of still larger sizes.

5. Summary

The specific heat of MgO at various temperatures from 50 to 850° absolute is computed by adding up the Einstein functions corresponding to the nine modes with discrete frequencies indicated by the dynamical theory and confirmed by infra-red spectroscopy. To this is added the contribution from a residual spectrum of vibrations of lower frequencies, the existence of which is also indicated by the dynamical theory. A very satisfactory agreement emerges over the whole range of temperatures between the calculated and observed specific heats.

The spectroscopic behaviour of rock-salt and the evaluation of its specific heat—Part I. The structure and its free vibrations

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1. Introduction

Sodium chloride, as is well known, crystallises in the cubic system and is therefore optically isotropic. If the material is pure, the crystals are colourless and transparent over a wide range of wavelengths in the spectrum. The absorption is negligible between $0.2\ \mu$ and $10\ \mu$, and is quite small between $10\ \mu$ and $15\ \mu$, but increases rapidly as we proceed further out into the infra-red. The technical possibility of preparing crystals of the material in large sizes from melts and of cutting out prisms from such material has made rock-salt play a highly important role in the development of infra-red spectroscopy. The range of wavelengths covered by recording instruments using NaCl prisms is from $1\ \mu$ to $15\ \mu$.

The simplicity of the composition and structure of rock-salt and the ready availability of the material make its physical properties, including especially its optical and spectroscopic behaviour, matters of very great interest from a theoretical point of view. Quite naturally, therefore, a great volume of literature exists describing the results of experimental studies and also of theoretical discussions concerning these matters. In the present memoir we are concerned with the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths and its relation to the crystal structure and thermal properties of the material. It is, therefore, appropriate that we briefly recall here the major facts which have emerged from the experimental researches on the subject.

Three different methods are available for the study of the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths. The first is that of determining the variation of the reflecting power of rock-salt in the region of great wavelengths. Earlier investigations indicated that the reflecting power is quite small up to about $35\ \mu$ and that it commences to rise steeply beyond $40\ \mu$. It exceeds 80% between $50\ \mu$ and $55\ \mu$, and then drops to 70% at $60\ \mu$ and to 40% at $70\ \mu$. The further diminution at still greater wavelengths is relatively more slow.

The more recent investigations indicate a reflecting power greater than 90% between $50\ \mu$ and $56\ \mu$, and also reveal additional features in the region of lower wavelengths which will be referred to later.

The second method is the study of the absorption of infra-red radiation in its passage through the material. The spectral transmission curve depends very much on the thickness of material traversed. The absorption coefficient which is small at $15\ \mu$ increases more and more steeply with increasing wavelength as we approach the region in which the reflecting power becomes large. In the latter region, the cut-off due to the reflection at the two surfaces of the plate is superposed upon the loss due to absorption. To obtain any sensible transmission in this region, very small thicknesses of the material are needed. Very interesting results were obtained and reported by Czerny (1930). Mentzel (1934) observed that the curve of percentage transmission through a rock-salt plate $24\ \mu$ thick showed an arrest between $34.5\ \mu$ and $35.5\ \mu$, the curve running horizontally between these wavelengths though it goes down steeply with increasing wavelength both above and below this range. Barnes and Czerny (1931) found that the curve of transmission through a plate $8\ \mu$ thick likewise runs horizontally in the wavelength range between $40\ \mu$ and $44\ \mu$. These authors also studied the transmission through evaporated films of NaCl of various thicknesses between $3.6\ \mu$ and $1.35\ \mu$. The percentage transmission exhibited as a graph in their paper shows two downward dips located at $40\ \mu$ and $50\ \mu$ respectively, besides the highly pronounced minimum of transmission around $60\ \mu$. The thinner films showed a further small dip in the transmission curve at about $71\ \mu$. Mentzel in his paper listed $34\ \mu$, $40.5\ \mu$ and $51\ \mu$ as minor maxima of absorption and $61.1\ \mu$ as the major absorption wavelength for NaCl. He also listed $33\ \mu$, $41\ \mu$, $42.5\ \mu$, $47\ \mu$ and $60\ \mu$ as minor absorption peaks and $70.7\ \mu$ as the major absorption wavelength for KCl. The appearance of a whole series of minor absorption peaks is thus evidently a characteristic feature of the spectroscopic behaviour of the alkali halides.

A third and very powerful method for the study of the spectroscopic behaviour of rock-salt was initiated and employed by Rasetti (1931). The transparency of the crystal in the ultra-violet region enables the powerful $2536.5\ \text{\AA}$ radiation emitted by a water-cooled and magnet-controlled mercury arc to be used for illuminating the interior of the solid and for recording the spectrum of the scattered radiation emerging from its interior. Rasetti made the noteworthy discovery that the spectrum thus recorded exhibits a sharp and intense line with a wave-number shift of $235\ \text{cm}^{-1}$ from the exciting radiation. This is the most conspicuous feature observed in the spectrum which commences with a sharp rise in intensity from zero to a large value at the wave-number shift at $360\ \text{cm}^{-1}$ and extends towards smaller frequency-shifts. The drop of intensity beyond the sharply-defined peak of the line at $235\ \text{cm}^{-1}$ to zero in the region of smaller frequency-shifts is also quite steep but is broken by the presence of a feeble band which covers the region of frequency-shifts between $220\ \text{cm}^{-1}$ and $184\ \text{cm}^{-1}$. The upper end of the spectrum exhibits a peak of intensity which is both smaller and not so well defined

as the line at 235 cm^{-1} and covers the region of frequency-shifts between 360 cm^{-1} and 340 cm^{-1} . Clearly separated from both of these principal features in the spectrum and approximately midway between them appears a group of four maxima of intensity located respectively at the frequency-shifts of 314 cm^{-1} , 300 cm^{-1} , 280 cm^{-1} and 258 cm^{-1} . These are clearly separated from each other in the spectrum as well as in its microphotometer record.

It is proposed in this memoir to consider the spectroscopic behaviour of rock-salt in its fundamental aspects and also in relation to its activity in infra-red absorption and reflection and its activity in the scattering of light with change of frequency. A satisfactory explanation is given for the facts established by experimental study in both of these fields of research. The thermal energy content of rock-salt and the variation of its specific heat with temperature also receive a quantitatively satisfactory explanation in terms of the spectroscopic properties of the crystal.

2. The structure of rock-salt

All crystals may be described as assemblages of two kinds of particles differing in their nature and properties, being respectively the heavy positively charged nuclei and the light negatively charged electrons. These two types of particles by reason of their mutual interactions hold each other in place and form a regularly arranged grouping in space. The massive nuclei are located at specific points in the structure but are capable of executing oscillatory movements about those positions. On the other hand, since the mass of the electrons is very small, they are appropriately described as forming a cloud which envelops the nuclei and fills up the volume of the solid. The attraction of a nucleus on the electrons in its immediate vicinity results in a closer association between them. As a consequence, the field due to each positive charge is more or less completely cancelled out at a distance from it. Part of the electronic cloud however remains subject to the influence of more than one nucleus and this plays a highly important role in holding the crystal together as a coherent solid. The physical properties of the crystal and especially its spectroscopic behaviour in the lower ranges of frequency are largely determined by it.

The numbers of Na and Cl nuclei in rock-salt are equal and their dispositions in the structure are very similar. The usual description of the structure is that it consists of two interpenetrating face-centred cubic lattices, the points of which are occupied respectively by Na and Cl nuclei. Each Na nucleus appears surrounded by six Cl nuclei and each Cl nucleus by six Na nuclei, the distance between the nearest neighbours being one-half of the edge-length of the cubic cell as measured from one Na nucleus to the next or from each Cl nucleus to the next. In the atomic layers parallel to the cubic faces of the crystal, the Na and the Cl nuclei appear interspersed in such manner that each Na nucleus has four Cl nuclei as its

immediate neighbours, while each Cl nucleus has four Na nuclei similarly situated with respect to it. On the other hand, in the atomic layers which are equally inclined to all the cubic axes, in other words are parallel to the faces of the octahedron, the Na nuclei and Cl nuclei do not appear together but are located in separate but equidistant layers. The distance a between neighbouring Na and Cl nuclei is also the spacing of successive atomic layers parallel to the cubic faces, while the separation of each Na layer from either of the two Cl layers adjacent to it in the octahedral planes is $a/\sqrt{3}$.

The structure of rock-salt may also be described as arising from the juxtaposition of two rhombohedral lattices displaced with respect to each other, the points of the two lattices being occupied respectively by Na and by Cl nuclei. Eight nuclei occupying the corners of a rhombohedron delineate the cells of each lattice. Six of them are located at the face-centres of a cube while the remaining two are located at opposite cube-corners.

3. The free vibrations of the structure

The atomic nuclei being enormously more massive than the electrons, it is permissible, when we seek to find and enumerate the normal modes of vibrations of the nuclei about their positions of equilibrium in the structure, to regard the electrons as being in the nature of massless elastic springs holding the nuclei in their places. Since the crystal also consists of an enormous number of similar and similarly situated structural units each containing its quota of atomic nuclei which is the same for all the structural units, we may justifiably adopt the following procedure in dealing with the problem. We proceed on the basis of the theorem in the classical mechanics which states that the small vibrations of a system of connected particles about their positions of equilibrium are a summation of a set of normal modes in each of which all the particles of the system vibrate in the same or opposite phases, while the total number of normal modes is the same as the number of degrees of dynamical freedom of the system of particles. It follows that the vibrations of the atomic nuclei should satisfy the following two requirements: in any normal mode, the nuclei should all vibrate in the same or opposite phases; a normal mode should remain a normal mode following a unit translation of the crystal along any one of the three axes of the crystal structure. Taking these two principles together, it follows as a necessary consequence that following a unit translation of the crystal, the atomic nuclei in the structural unit would retain the same amplitudes of vibration while their phases would either *all* remain unaltered or else would *all* be reversed. Thus, we have two species of normal modes satisfying the requirements for each of the three axes of the structure, and since these possibilities are independent, we have $2 \times 2 \times 2$ or 8 species of normal modes in all.

We may readily apply these results to the case of a simple rhombohedral lattice at whose points only one kind of nucleus is located. Each of the 8 species of

normal modes corresponds to a different disposition of the phases of vibration of the 8 nuclei situated at the corners of the cell. As each nucleus has three degrees of dynamical freedom, we have 24 available degrees of freedom. The nature of the 24 different possible movements allowed by these degrees of freedom can be readily ascertained by considering the different combinations of the phases of vibrations of the nuclei located at the points of the rhombohedral lattice. Three of them are movements of all the nuclei in the same phase, in other words, simple translations of the whole group of nuclei. Nine of them represent movements in which the nuclei lying in the same cubic plane move in the same phase while those in the adjoining cubic planes move in the opposite phase. The remaining twelve represent movements in which the nuclei lying in the same octahedral plane move in the same phase while those lying in the adjacent octahedral plane move in the opposite phase. These two groups may be further sub-divided by considering the directions of movement indicated by the cubic symmetry of the whole structure. Thus the 24 possible movements may be listed as below, it being noted that the oscillations of the nuclei located in the successive planes (cubic or octahedral as the case may be) are in opposite phases.

1. Simple translations	3
2. Oscillations normal to the cubic planes	3
3. Oscillations tangential to the cubic planes	6
4. Oscillations normal to the octahedral planes	4
5. Oscillations tangential to the octahedral planes	8
	Total
	24

Thus, the 24 degrees of dynamical freedom of the group of 8 nuclei located at the corners of the rhombohedral cell are duly accounted for, 3 of them as simple translations and the remaining 21 as normal modes which fall into four groups with degeneracies 3, 6, 4 and 8 respectively, arising by reason of the cubic symmetry of the structure.

In the rock-salt structure we are concerned with two sets of nuclei (Na and Cl respectively) occupying the points of two similar rhombohedral lattices. Hence the foregoing description would apply to each of them. The phases of oscillation of the Na and Cl nuclei in each of the 24 modes may be either the same or opposite. Hence, we have 48 normal modes in all, corresponding to the 48 degrees of dynamic freedom of a group of 16 nuclei, 8 of Na and 8 of Cl. The three translations of each lattice separately are replaced by three translations in which the two lattices move together in the same phase, and by three oscillations respectively along the three cubic axes of the two lattices moving in opposite phases, the movement of the Na nuclei being balanced by the movement of the Cl nuclei in the contrary direction. Besides these, we have *four modes* which are coupled oscillations of the Na and Cl nuclei, two being normal and two tangential to the cubic planes with the Na and the Cl nuclei in those planes moving

respectively in the same or in the opposite phases with respect to each other; also *four modes* in which the *Na nuclei alone* or the *Cl nuclei alone* present in the octahedral planes oscillate respectively normal and tangential to those planes.

4. The normal modes of vibration

The nine normal modes of vibration and the three residual translations are listed below as a table:

	Degeneracy
I. Oscillation of the Na and Cl lattices in opposite phases	3
II. Coupled oscillations of the Na and Cl nuclei in the cubic planes:	
(a) Tangential to the planes in opposite phases	6
(b) Normal to the planes in the same phase	3
(c) Normal to the planes in opposite phases	3
(d) Tangential to the planes in the same phase	6
III. Oscillations of the nuclei appearing in the octahedral layers:	
(a) Na nuclei normal to the planes	4
(b) Na nuclei tangential to the planes	8
(c) Cl nuclei normal to the planes	4
(d) Cl nuclei tangential to the planes	8
IV. Translations of both lattices in the same phase	3
Total	48

The nine modes have been numbered and shown in the table in a particular order for reasons which will presently be explained. Figures 1, 2 and 3 in the text below illustrate the character of the oscillations in each case, the numbering of the figures following the same order as in the table. The hatched circles represent the Na nuclei and the open circles the Cl nuclei. Figures 1 and 2 represent the structure viewed along a cubic axis; the cubic layers depicted are assumed to be horizontal, and the arrows represent the movements of the nuclei. Figure 3 is a view of the structure in a direction which is the intersection of an octahedral plane with a diagonal plane of the cube. It exhibits the Na and the Cl nuclei as appearing in distinct layers parallel to the faces of the octahedron.

5. The frequencies of the normal modes

It would obviously be useful if the nine modes of vibration described and pictured above can be arranged in descending order of frequency, as this would greatly

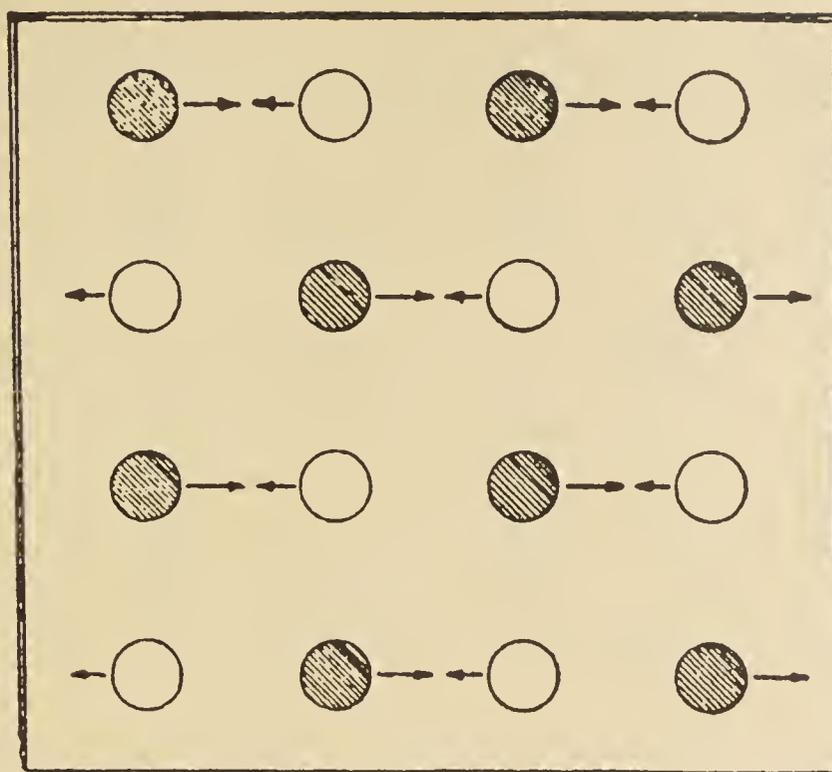


Figure 1. Oscillation of the Na and the Cl lattices in opposite phases.

facilitate the comparison with the spectroscopic data and a definitive determination of their frequencies.

The mode illustrated in figure 1 evidently stands apart in a category by itself. This oscillation repeats itself from cell to cell, whereas in all the other eight modes the phase of vibration alternates from layer to layer. It may therefore be safely presumed that figure 1 represents the mode of highest frequency. The coupled oscillations of the Na and Cl nuclei in the cubic planes have been listed and pictured in the order of figures 2(*a*), (*b*), (*c*) and (*d*). This would clearly also represent their arrangement in descending order of frequency. For, the movement in figure 2(*a*) most closely resembles that in figure 1 and the movement in figure 2(*b*) rather less closely, while the movements in figures 2(*c*) and 2(*d*) are clearly of a different nature. Indeed, figure 2(*d*) closely resembles a transverse oscillation of the cubic layers as a whole and hence should have the lowest frequency of the four modes and indeed also of all the nine modes.

Since the masses of the Na nuclei are much smaller than those of the Cl nuclei, it is evident that the modes depicted in figures 3(*a*) and 3(*b*) would both have higher frequencies than the modes shown in figures 3(*c*) and 3(*d*). The mode shown as figure 3(*a*) would evidently have a higher frequency than the mode shown as figure 3(*b*), since the Na layers approach each other normally in one case and move tangentially to each other in the other case. Likewise, the frequency of mode III(*c*) would be higher than that of mode III(*d*). But the differences between the normal and tangential modes in either case would not be very large for the reason that the six nearest neighbours of each oscillating nucleus are situated symmetrically around it and hence its interactions with them would be the same in both cases.

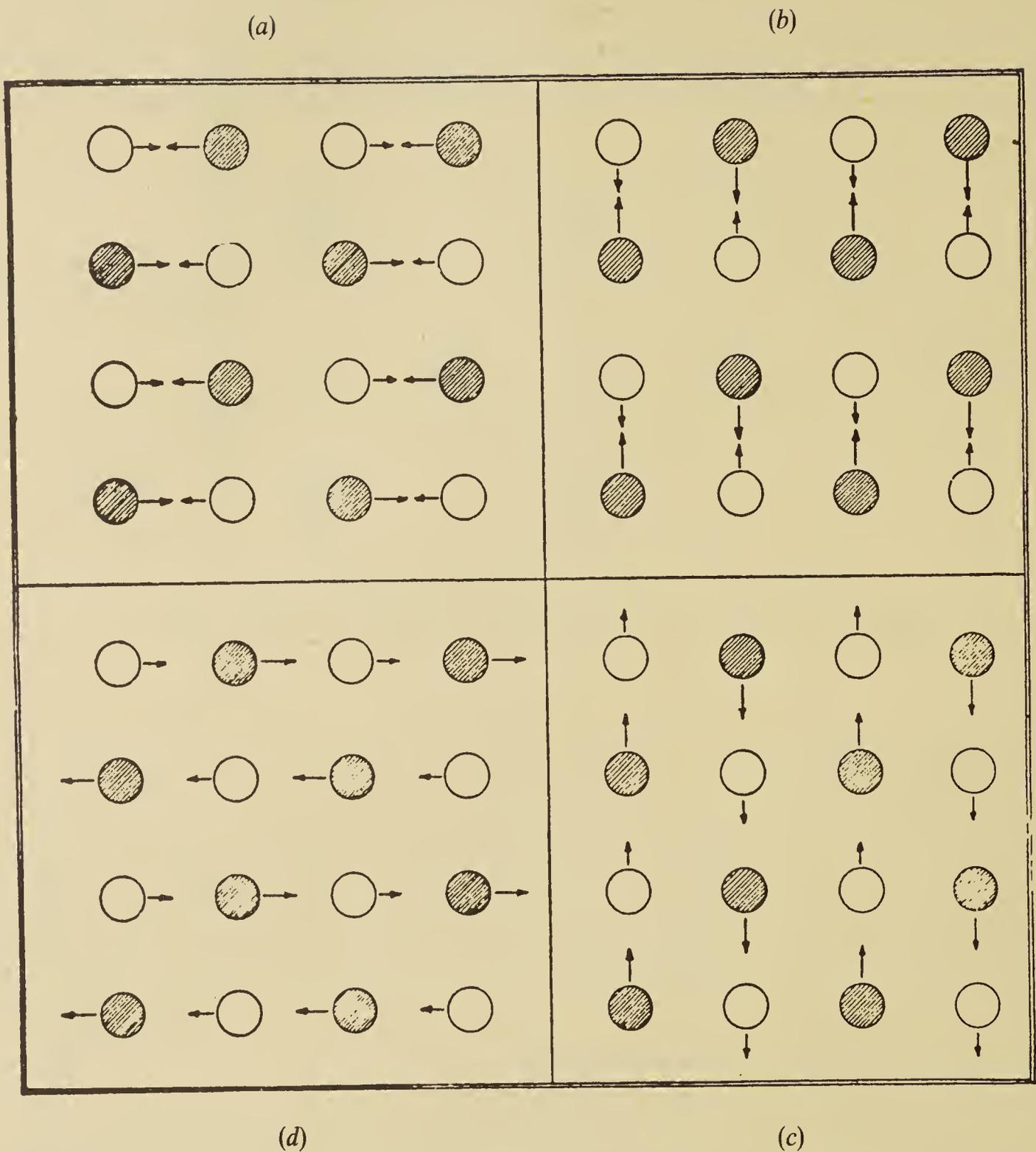


Figure 2. (a), (b), (c) and (d): Coupled oscillations of the Na and Cl nuclei in the cubic layers.

6. Approximate evaluation of the frequencies

We may go a little further and make a rough computation of the frequencies of all the nine modes on the basis of a simplified picture of the internuclear forces which are operative in a vibration. We notice that in figure 1 the movements are along a cubic axis of the crystal and represent an approach of a Na nucleus to the Cl nucleus which is its nearest neighbour on one side and a recession from the Cl nucleus on the other side. (We may interchange the Na and the Cl nuclei in this description.) The forces brought into play would be principally those resisting

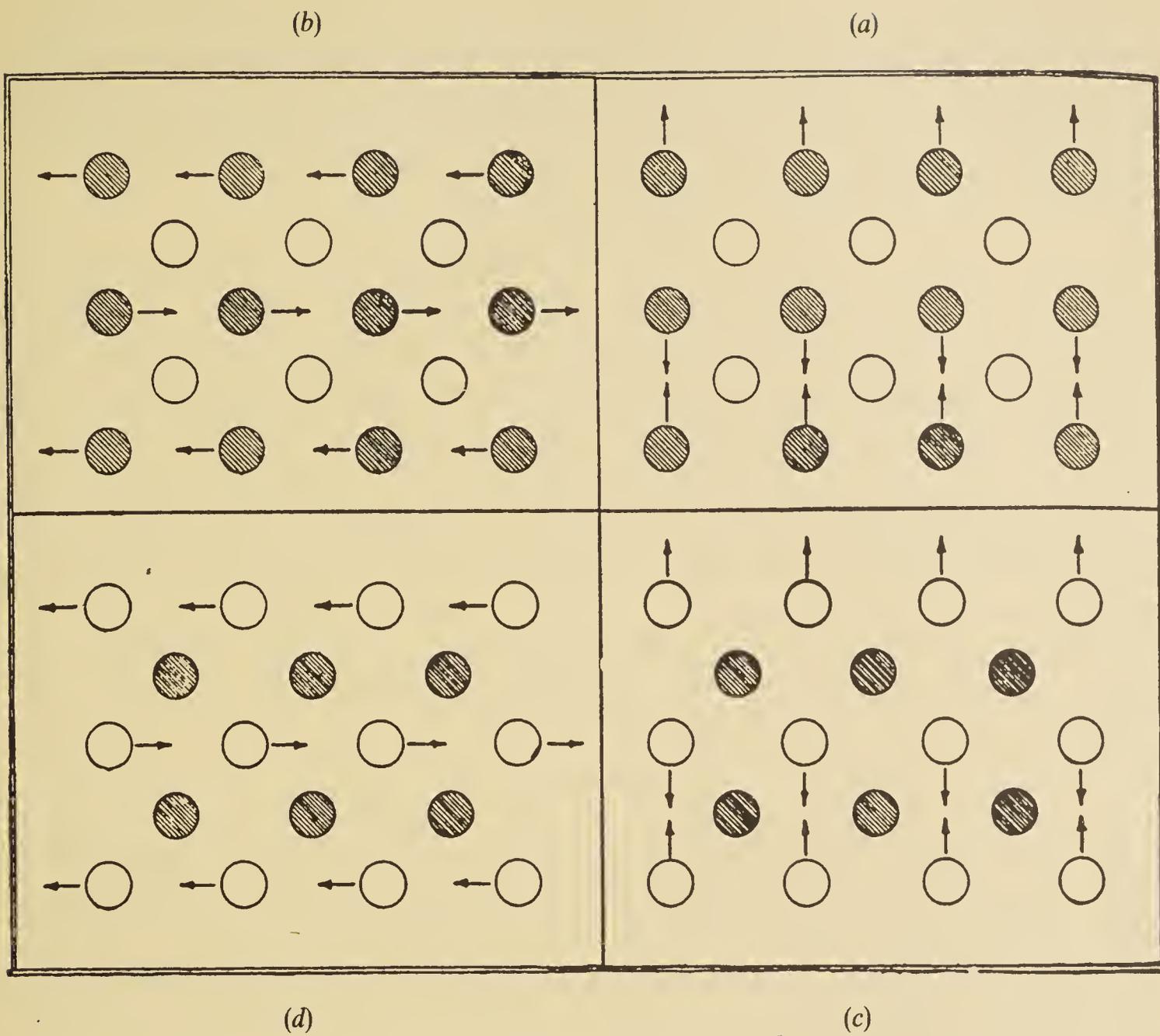


Figure 3. (a), (b), (c) and (d): Oscillations of the Na and the Cl nuclei in the octahedral layers.

such approach or recession. Of lesser importance would be those resisting the transverse displacement of each Na nucleus with respect to the four other Cl nuclei which are also its nearest neighbours on the perpendicular cubic axes. We shall assume these forces to be respectively proportional to the relative displacements, the constants of proportionality being α and β respectively. We neglect all other interactions. Such neglect is fully justified as regards interactions with more distant nuclei *of the same species*, since they move with the same amplitudes and phases. Writing down the equations of motion of two adjoining nuclei (Na and Cl respectively) and solving them, we find that the circular frequency of the vibrational mode I is given by

$$\omega_1^2 = (2\alpha + 4\beta)(1/m_1 + 1/m_2),$$

where m_1 and m_2 are respectively the masses of the Na and Cl nuclei.

Considering only the interactions between each Na nucleus and the surrounding six Cl nuclei, and vice versa, the equations of motion may be written down and solved for the two modes represented in figures 2(a) and 2(d). The circular frequencies of these modes may be found on evaluating the two roots of the equation which is obtained as the solution, viz.,

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 16\beta(\alpha + \beta)/m_1 m_2 = 0.$$

Likewise, on the same basis, the equations of motion for the two modes represented by figures 2(b) and 2(c) may be written down and solved. Their circular frequencies may be found from the two roots of the equation

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 32\alpha\beta/m_1 m_2 = 0.$$

It will be noticed from these equations that the frequencies of the two coupled oscillations in each case are related to the frequency ω_I of mode I by the simple relations

$$\omega_{II} a^2 + \omega_{II} d^2 = \omega_I^2$$

and

$$\omega_{II} b^2 + \omega_{II} c^2 = \omega_I^2.$$

It is evident also from these relations that mode I has the highest frequency of all the five modes considered. They can all be computed if the values of α and β are known. Alternatively, if the frequency of mode I is known and some reasonable assumption is made for the ratio α/β , as for example that $\alpha = 2\beta$, the frequencies of the four other coupled oscillations of the Na and Cl nuclei can be found from that of the mode of highest frequency.

Assuming that the frequency of mode I expressed in wave-numbers is 180 cm^{-1} and that $\alpha = 2\beta$, we find the following values for the frequencies of the four other modes also in wave-numbers:

Frequency of mode I (assumed)	180 cm^{-1}
Frequency of mode II(a) (calculated)	158 cm^{-1}
Frequency of mode II(b) (calculated)	140 cm^{-1}
Frequency of mode II(c) (calculated)	113 cm^{-1}
Frequency of mode II(d) (calculated)	87 cm^{-1}

Thus, the descending sequence of frequency in which these five modes were arranged in the table and numbered in the figures is seen to be correct. It should be remarked however that the calculations ignored the interactions between each nucleus and the others of the same species present in the adjacent layers and moving with the same amplitude but in an opposite phase. As these nuclei are however situated further from it than the nuclei whose interactions have been considered, the calculations of frequency cannot be seriously in error. But they can only be considered only as approximations.

Considering now the four modes pictured as figures 3(a), (b), (c) and (d) it is obvious that their frequencies would be very simply related to that of mode I, provided that we take into account only the interactions between each Na nucleus and the six Cl nuclei around it, and vice versa. The relevant formulae are:

$$\omega_{\text{III}}^2 = (2\alpha + 4\beta)/m_1$$

for the modes III(a) and III(b) and

$$\omega_{\text{III}}^2 = (2\alpha + 4\beta)/m_2$$

for modes III(c) and III(d). If we take the frequency of mode I as 180 cm^{-1} in wave-numbers, that of modes III(a) and III(b) come out as 140 cm^{-1} and that of modes III(c) and III(d) as 113 cm^{-1} . This procedure for deducing the frequencies results in the modes of vibration tangential and normal to the octahedral planes having the same value. This is a consequence of our having neglected the interactions between the nuclei of the same kind which are in relative movement and hence would influence the frequencies of the vibration. As will be seen from figures 3(a), (b), (c) and (d), the adjacent layers of similar nuclei slide past each other in the tangential modes, while they alternately approach and recede from each other in the normal modes. The interactions between the moving layers would, in these circumstances, not be negligible. Their influence on the frequencies of vibration would evidently be greater in the normal modes than in the tangential ones, thereby making the frequencies in these cases different. It is also evident that the frequencies of 140 cm^{-1} and 113 cm^{-1} as computed and shown above would be slightly smaller than the correct values for the tangential modes, and definitely less than the correct values for the normal modes. Each moving nucleus comes under the influence of six nuclei of the same kind and six nuclei of the other kind in its movement, the distances between the interacting nuclei being $2a/\sqrt{3}$ and a respectively. In these circumstances, an increase of say 10% in the frequencies of the tangential modes and say 20% in the frequencies of the normal modes may be hazarded as a rough estimate of an alteration in the calculated frequencies produced by taking the interactions between like nuclei also into account.

7. Summary

The nine normal modes of free vibration of the rock-salt structure have been deduced theoretically and fully described. They have been arranged in descending order of frequency and an approximate estimate of their frequencies is also given. The mode of highest frequency is that in which the Na and Cl lattices oscillate in opposite phases.

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The spectroscopic behaviour of rock-salt and the evaluation of its specific heat—Part II. Its infra-red activity

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1. Introduction

The basic questions in relation to the infra-red activity of crystals are, *firstly*, how does the activity arise and *secondly* how is it related to the structure of the crystal? Since these two questions are closely connected, it is evident that answers to them could most appropriately be sought for in relation to crystals of the simplest possible structure and composition and of the highest possible symmetry. For, the various complications such as those arising from the details of molecular structure, molecular anisotropy and molecular interactions would be avoided and the questions requiring answer would present themselves in the most definite and tractable form. It is also essential that the case considered is one which could be most completely explored by spectroscopic methods and experimental data obtained which could be compared with the consequences of theory. NaCl is a case in which these requirements are satisfied and hence is very suitable as a test-case.

Infra-red activity manifests itself in three different ways which are susceptible of experimental study. Firstly, we have the refractivity of the material which as we pass from the visible into the infra-red region clearly exhibits the effect of infra-red activity. Secondly, we have the reflecting power of crystal surfaces, and thirdly, the absorption of radiation in its passage through the material. The absorption is a mass-effect and where it is very powerful as in the case of rock-salt, we could scarcely expect studies of it to reveal its relationship to the spectroscopic behaviour in an obvious fashion. It is indeed necessary to obtain spectrographic records of the percentage transmission by plates whose thickness is varied step by step over the widest possible range and to make a comparative study of the records in order to obtain any useful indications.

In the present memoir, we shall cover various aspects of the subject. Firstly, we shall consider it from a purely fundamental and general standpoint. Secondly, we shall discuss the relation between infra-red activity and the free vibrations of the

structure as considered in the first part of the memoir. Thirdly, the results of experimental studies of the kind indicated in the foregoing paragraph will be presented. Lastly, these experimental results will be correlated with those of Czerny and collaborators mentioned in the first part of the memoir and then compared with the consequences of theory.

2. The origin of infra-red activity

Viewed from the point of view of classical mechanics, the absorption of infra-red waves in their passage through a crystal can be considered as a transfer of energy which is effected by the electric field of the waves acting on the charged particles in its structure and setting them in vibration. If the frequency of the field is sufficiently close to the frequency of a normal mode of vibration, the possibility of resonance arises. But whether such resonance would actually occur is a question that needs examination.

As there are two types of charged particles in the structure, viz., the nuclei and the electrons, it is appropriate at first to consider the effects of the radiation field on them separately. The nuclei besides being positively charged possess masses enormously large compared with those of the electrons. It is a familiar consequence of classical mechanics that in a normal vibration the common centre of inertia of the particles of the system remains at rest. Likewise, in our present problem, the common centre of inertia of all the nuclei included in the vibrating structural unit would remain at rest in any free vibration. Hence, when all the nuclei have the same mass, as for example, in a crystal of diamond or silicon or germanium, the common centre of the positive charges carried by the nuclei would remain undisturbed during the vibration. It follows that when the crystal is traversed by infrared radiation, the forces exerted by the field on the positive charges would in the sum total be unable to transfer energy to the crystal and hence they could not possibly excite such vibrations. The situation would be the same even when the nuclei in the crystal belong to different species, provided that the ratio of the masses to the charges is the same for the different nuclei, as is the case for example with rock-salt or quartz. It follows that the positive charges of the nuclei do not play any role in the infra-red activity of the crystals. *All the observed effects arise from the action of the field of incident radiation on the negatively charged electronic clouds.*

The question then arises why the infra-red absorption spectra of a crystal should be related in any way or bear any resemblance to the spectrum of free vibrations of the atomic nuclei considered in the first part of the present memoir. The answer to this is that there is a connecting link between the infra-red absorption and the vibration spectrum of the atomic nuclei. This is to be found in the fact that the electronic clouds are held in the crystal by their interactions with the positively charged nuclei; vice versa the nuclei are held in their places by their

interactions with the electronic clouds. Hence, a periodic disturbance of the electronic clouds produced by the field of the radiation *may* tend to disturb the nuclei from their positions and set them in synchronous vibration. Vice versa, vibrations of the nuclei *may* tend to disturb the electronic clouds and set them in synchronous vibration. A periodic movement of the electronic cloud is a *sine qua non* for the production of the effects described under the term of infra-red activity. Hence, unless a free vibration of the nuclei is associated with and gives rise to such a movement of the electronic clouds, it would not be set up under the action of the periodic external electric field.

The foregoing discussions, apart from emphasising the fundamental role played by the electrons in the absorption of infra-red radiation and other related effects, make it clear why the *asymmetry* of the nuclear vibrations plays such a highly important role in infra-red activity. For, in the absence of such asymmetry, there would be no periodic displacement of the electronic clouds and hence no excitation of the nuclear vibrations.

3. Infra-red activity of the normal modes

From what has been stated in the preceding paragraph, it is clear that the four modes in which the Na nuclei alone or the Cl nuclei alone oscillate either normally or tangentially to the octahedral planes could not exhibit any infra-red activity. For, in these modes, two layers of Na nuclei approach or recede from an intermediate layer of Cl nuclei symmetrically on either side with equal amplitudes. Hence, the movements of electronic charges resulting therefrom when summed up over each of the structural elements of the crystal would vanish. This conclusion would be valid irrespective of the actual amplitude of the nuclear movements. Hence the four modes of the octahedral class can be disregarded in our consideration of the infra-red activity of the normal modes of vibration. We need only examine the behaviour of the five other normal modes in which the Na and Cl nuclei appearing in the cubic layers execute coupled oscillations.

The principal normal mode of highest frequency in which the Na and Cl lattices oscillate in a balanced movement stands in a class by itself and will therefore be considered first. By reason of the difference in the masses of the Na and the Cl nuclei, the amplitude of movement of the Na nuclei would be proportionately greater than that of the Cl nuclei and hence the amplitudes of oscillation of the electronic clouds respectively held by them in close association would also be different. But by reason of the difference in the positive charges of the two nuclei, the negative charge of the electrons so held would be smaller for the Na nuclei than for the Cl nuclei. The resulting displacements of negative charge when totalled up would therefore cancel out more or less completely. What would be left over and needs special consideration is the part of the electronic cloud which comes under the influence of both sets of nuclei and its

movements under the action of the field of incident radiation.

During one half-period of the oscillation, the Cl nucleus on one side of a Na nucleus approaches it and the Cl nucleus on the other side recedes from it. During the other half-period, these movements are reversed. It is clear, however, that the asymmetric displacements of electric charge with which we are here concerned would be in the same direction on both sides of the Na nucleus and that they would be reversed in successive half-periods of the oscillation. Hence, they would not cancel out but would add up to produce a periodic displacement of negative charge having the same frequency as the incident waves. Further, since the oscillation of the nuclei repeats itself from cell to cell, the effects of all the cells would add up and hence would result in a large effect. In other words, the normal mode of highest frequency would be powerfully infra-red active, and it would need only a very small thickness of the material to make such activity manifest. The coherent phase relationship between the oscillations of electric charge in the adjacent cells of the structure would have a further consequence. The oscillating electric charges at and near the surface of the crystal would act as secondary sources of radiation and their conjoint action would result in a powerful reflection of the incident radiation at the surface of the crystal. This effect would be most powerful at and near the frequency of the normal mode under consideration. For, at such frequencies, the movements of the nuclei would be most vigorous and hence the displacements of negative electric charge associated therewith would be large.

The four other modes of coupled oscillation of the Na and Cl nuclei stand on an entirely different footing. In these modes, the oscillation reverses its phase as it passes from one cubic layer of the crystal to the next. Hence, the displacements of electric charge would be in opposite phases in the alternate layers and when summed up would cancel each other out. Hence, these four normal modes would not exhibit any infra-red activity. This statement is however subject to various qualifications, since it rests on two assumptions. The first assumption is the complete independence of the normal modes of vibration. The second assumption is that the amplitudes of vibration are extremely small. If these assumptions are not valid, the conclusion drawn that the four normal modes are inactive would also need reconsideration.

4. Overtones of the normal frequencies

So far, we have proceeded on the basis of the theory of small vibrations of a connected system of particles in the classical mechanics. The curious feature of the case is that the forces which are effective in exciting the vibrations are not those acting on the masses, viz., the positively charged nuclei, but on the springs, viz., the negatively charged electrons which hold them together and effectively determine their frequencies of vibration.

We have now, of necessity, to introduce the fundamental notions of the quantum theory. The energy of the radiation appears in quanta proportional to its frequency and if such energy is to be completely taken up by the oscillators with which we are concerned, viz., the group of 8 Na and 8 Cl nuclei, the frequency of the mechanical oscillations should be the same as that of the incident radiation. In other words, we would have resonance. But we have also to consider the cases in which the frequency of the free vibration is not the same as that of the incident radiation. Of special interest are the cases in which the frequency of the incident radiation is a small multiple of the frequency of the oscillator, and hence the absorption of energy would involve the acceptance by the oscillator of two, three or larger number of quanta of the energy of radiation. It may be presumed that the probability of this happening would diminish rapidly with the increasing number of quanta thus taken up, in other words that the absorption would then become rapidly weaker and weaker in the series. But since we are dealing with a crystal, there should be no difficulty in observing such absorption. We have only to increase the thickness of the absorbing plate sufficiently to be able to record the absorption spectra of the higher orders.

The further question then arises, what is the factor which determines the diminishing strength of the absorption with the increasing number of quanta taken up by the oscillator? We may remark that an increase in the magnitude of the energy taken up involves an increase of the amplitude of the resulting vibration. The absolute dimensions of the oscillator being small, the amplitude of the movements corresponding only to one quantum of energy could by no means be considered as small, and the amplitude corresponding to two, three more quanta would far transcend any such limits. The movements of the electronic clouds which are the operative cause of infra-red activity would become more and more nearly comparable with the dimensions of the electronic clouds more closely associated with the Na and the Cl nuclei. It would clearly, in these circumstances, cease to be justifiable to assume that the classical theory of small vibrations and its consequences would correspond with the facts of experiment. In other words, the appearance of overtones of the normal frequencies in absorption and the diminishing strength of such absorption with increasing frequency are both associated with the increasing amplitude of the resulting vibrations and the consequence arising therefrom.

We have already noticed that the normal mode of highest frequency would exhibit infra-red activity with great strength. It follows that this mode would also exhibit infra-red absorption of the higher orders in a conspicuous manner. It is also evident that the absence of infra-red activity of the four other modes of coupled oscillation which was remarked upon earlier would not extend to absorption of the higher orders corresponding to frequencies which are multiples of the frequencies of free vibration in those modes. For, their inactivity in the first order absorption was ascribed to the opposition of the phase of the oscillation in the alternate layers of the structure in those modes. When the amplitudes are

large, the displacements of charge in one layer and in the next layer where the phase of the motion is opposite would not be numerically of equal magnitude and hence when they are summed up they would not cancel out completely. The residue would have twice the frequency of the oscillation. The octaves of these modes could therefore be expected to appear in absorption with considerable strength.

Another important consequence of the amplitudes of vibrations not being small is that the various normal modes would cease to be completely independent of each other. The sharpness of resonance which is a characteristic consequence of the theory of small vibrations would be notably departed from when, as in the present case, we have five normal modes which are spread over a wide range of frequencies and are not restricted to small amplitudes of vibration. In these circumstances, the energy of the incident radiation can be taken up for the excitation of vibrations which may be described as a superposition of two or more normal modes approximating to each other in frequency. It is also possible for a vibration to be excited which may be described as a superposition of one normal mode as a fundamental with another normal mode as an overtone with a frequency which is not very different. More generally, the radiation may excite vibrations which may be described as a summation of two or more normal modes differing from each other in frequency and either as fundamentals or as overtones.

Earlier, we discussed the reflection of infra-red radiation which occurs when the incident radiation has the same frequency as the normal mode of highest frequency. We have now to remark that reflections of notable strength may also arise at other frequencies in consequence of the incident radiation exciting superposed vibrations of the kind referred to above with sufficiently large amplitudes. We shall have occasion to consider such cases later in this memoir.

5. The absorption spectra of rock-salt

Some excellent specimens of transparent salt were available in the museum of the Institute and it appeared worthwhile to study their behaviour in absorption, making use of the Leitz infra-red recording spectrophotometer with KBr optics which covers the spectral range between 13μ and 24μ . This, of course, is much outside the wavelength range within which powerful infra-red reflections are exhibited by rock-salt. The considerations set forth above however indicate that the absorption spectra of the higher orders could be recorded within the range of the instrument and evidence thus obtained both for the existence of such absorption and its relation to the specific modes and frequencies of vibration of the atomic nuclei in the crystal. Nine different thicknesses of the absorbing material ranging from 5.2 cm down to 1.5 mm were employed and their transmission percentages were recorded. A comparative study of the records reveals some very significant features. To illustrate them, the nine records are

reproduced below in the text as figures 1 to 9, the absorption path being indicated below each figure.

Figure 1 recorded with a block 5.2 cm thick exhibits nearly complete transparency at $13\ \mu$, followed by a progressive fall to opacity at $18.5\ \mu$, beyond

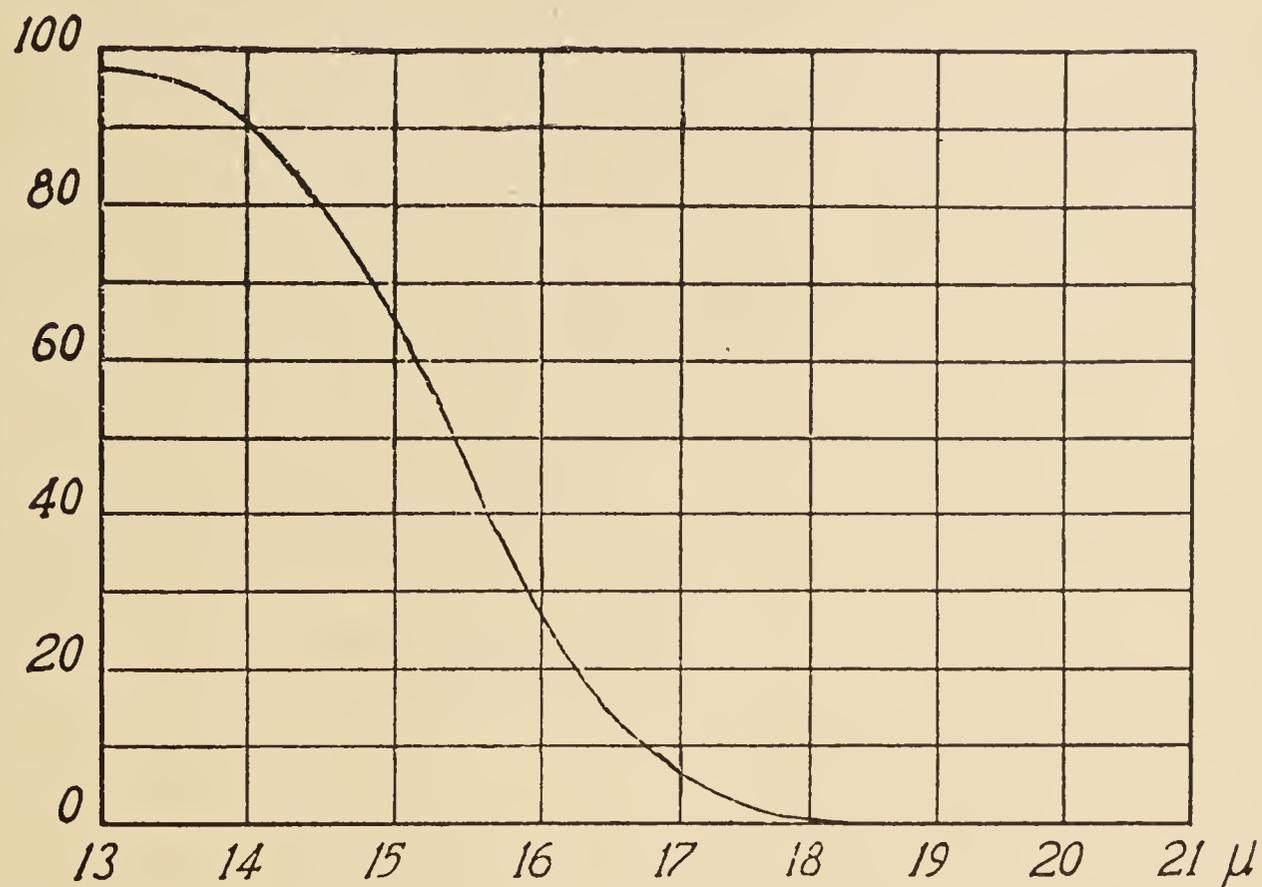


Figure 1. Infra-red absorption by rock-salt: 5.2 cm.

which there is a complete cut-off of all transmission. Very similar features are also exhibited in figures 2 and 3 which were recorded with blocks which were respectively 4.3 and 2.8 cm thick. It will be noticed, however, that a rapid improvement in transparency in the wavelength range between $13\ \mu$ and $14.5\ \mu$ appears as the absorption path is diminished. Whereas a difference of 18% in the transmissions at $13\ \mu$ and $14.5\ \mu$ is noticed in figure 1 for the block 5.2 cm thick, the difference is only 12% in figure 2 for a thickness of 4.3 cm and only 5% in figure 3 for a thickness of 2.8 cm. On the other hand, in the region of longer wavelengths, as will be seen on a comparison of figures 1, 2, 3, 4 and 5, there is little or no change in transmission produced by the large change in the absorption path from 5.2 to 1.5 cm. The cut-off of the longer wavelengths persists and the transmission at $19\ \mu$ is either zero or very small in all five cases. It is clear from the spectrographic records that the absorptions in the spectral regions from $13\ \mu$ to $19\ \mu$ and from $19\ \mu$ to $24\ \mu$ are of totally different orders of magnitude.

As is to be expected in the circumstances stated above, very striking changes appear in the form of the transmission curve when the thickness is greatly reduced and is of the order of a few millimetres only. Figures 6 to 9 are the records

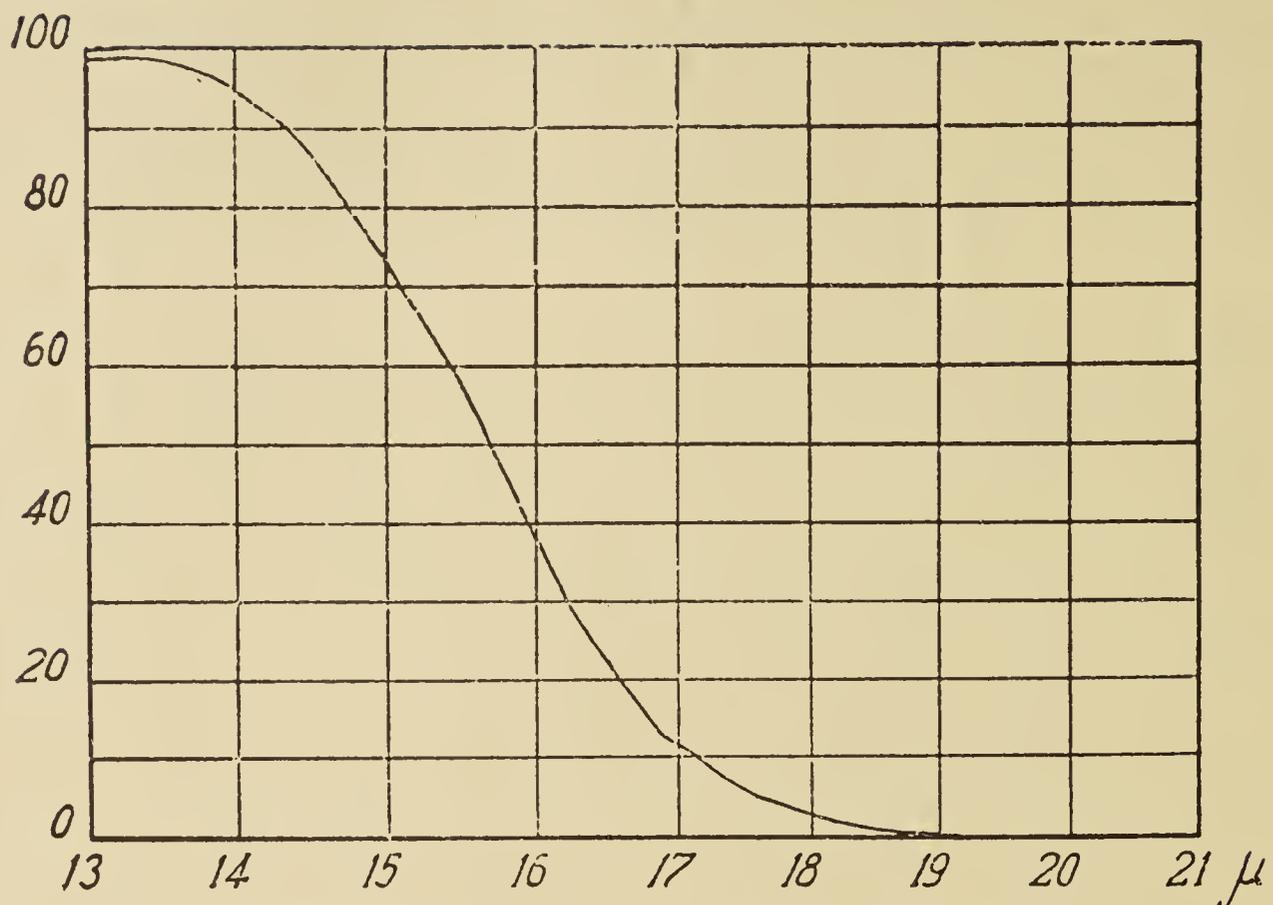


Figure 2. Infra-red absorption by rock-salt: 4.3 cm.

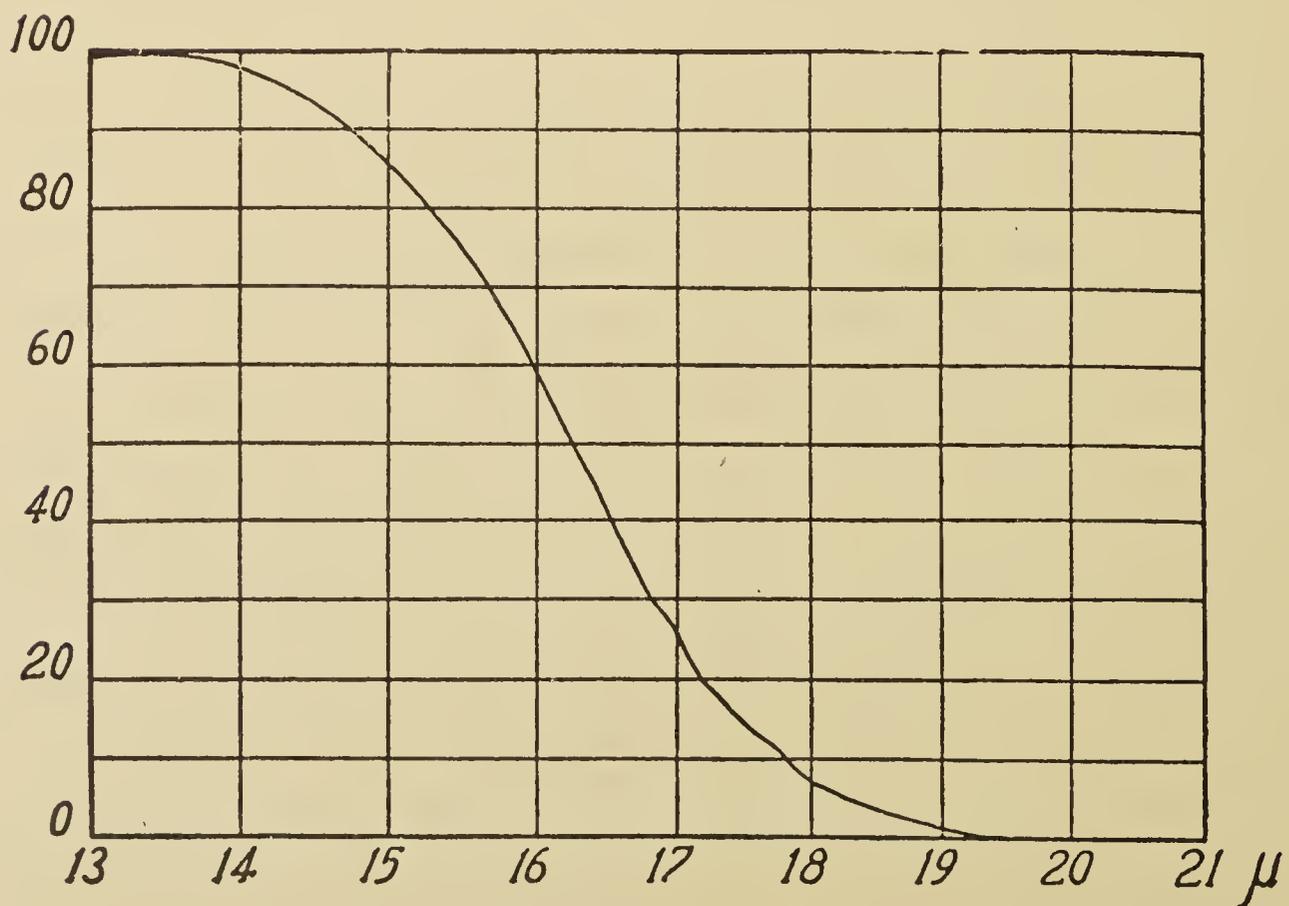


Figure 3. Infra-red absorption by rock-salt: 2.8 cm.

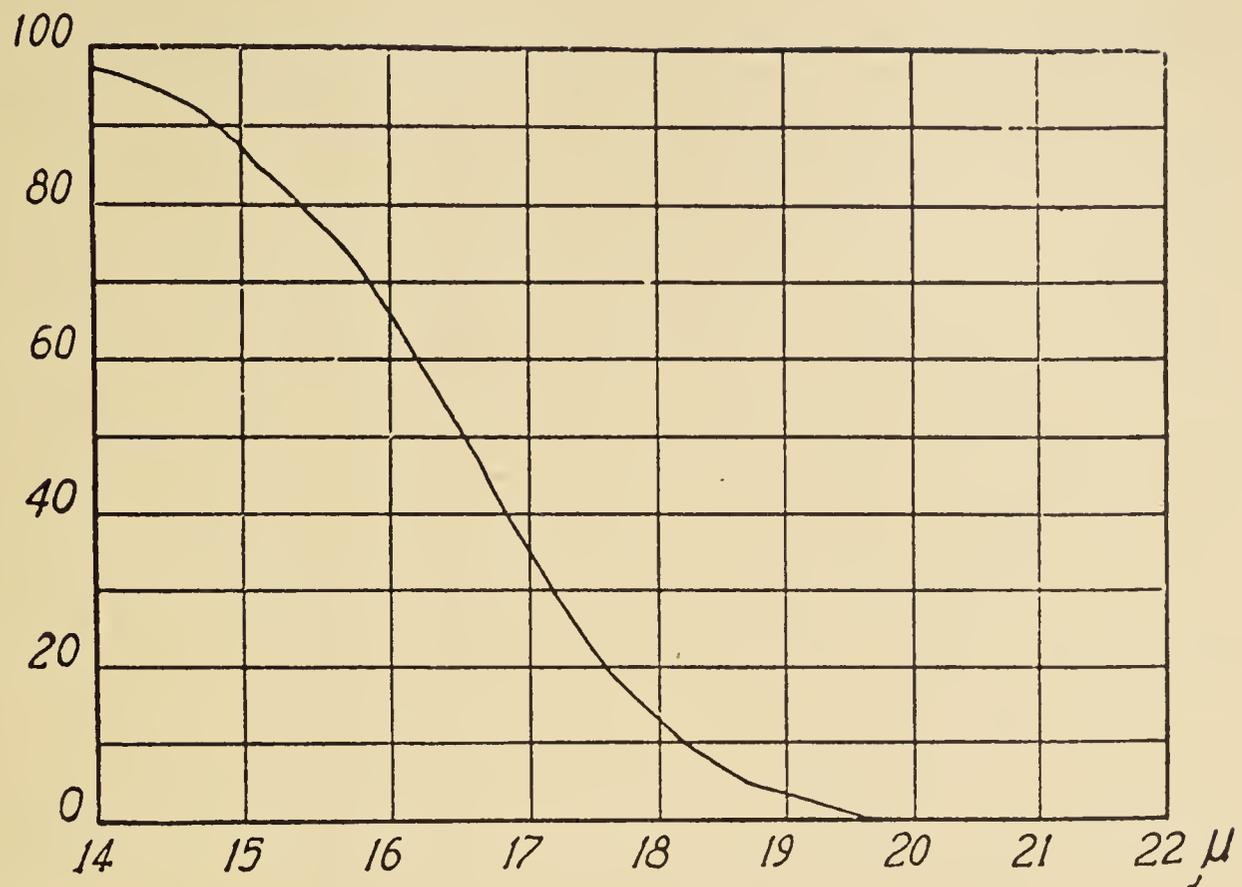


Figure 4. Infra-red absorption by rock-salt: 2.1 cm.

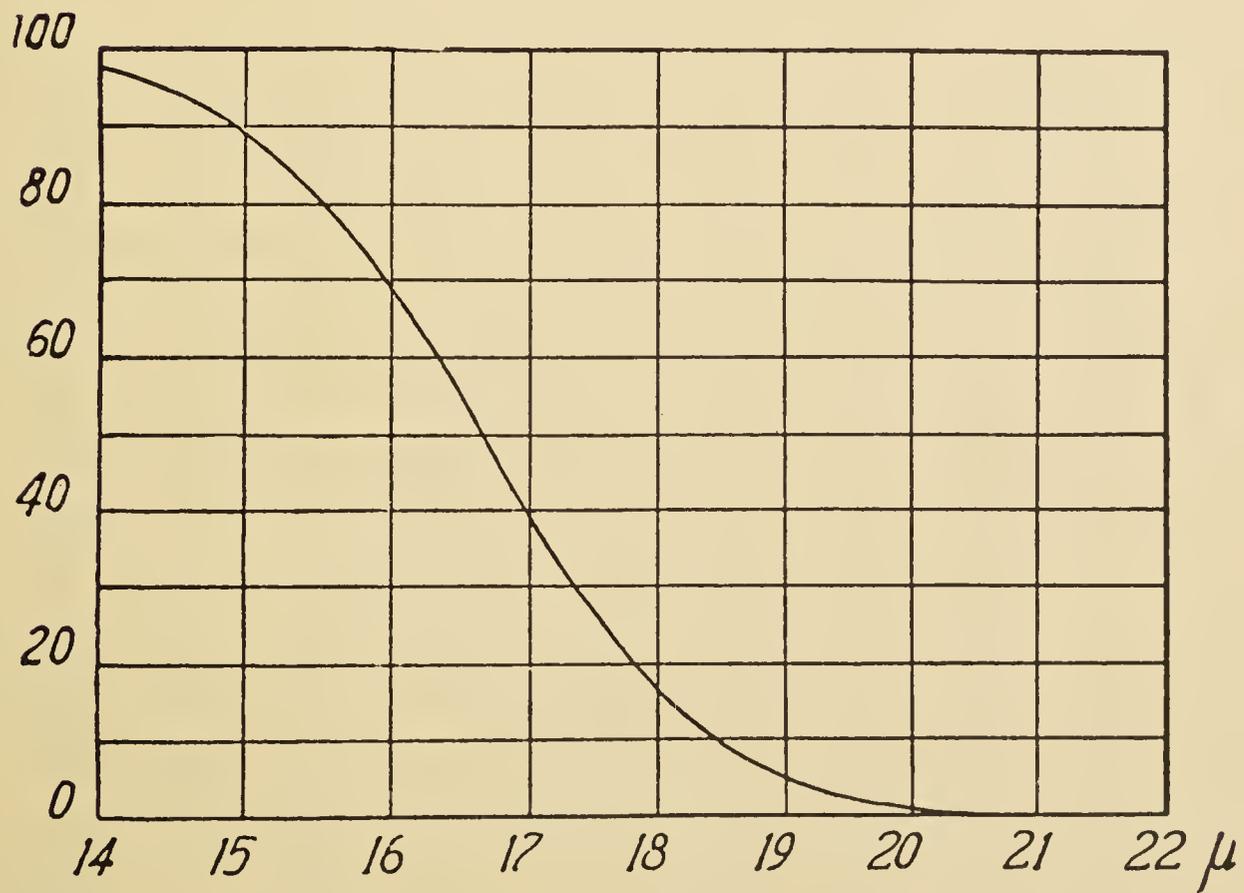


Figure 5. Infra-red absorption by rock-salt: 1.5 cm.

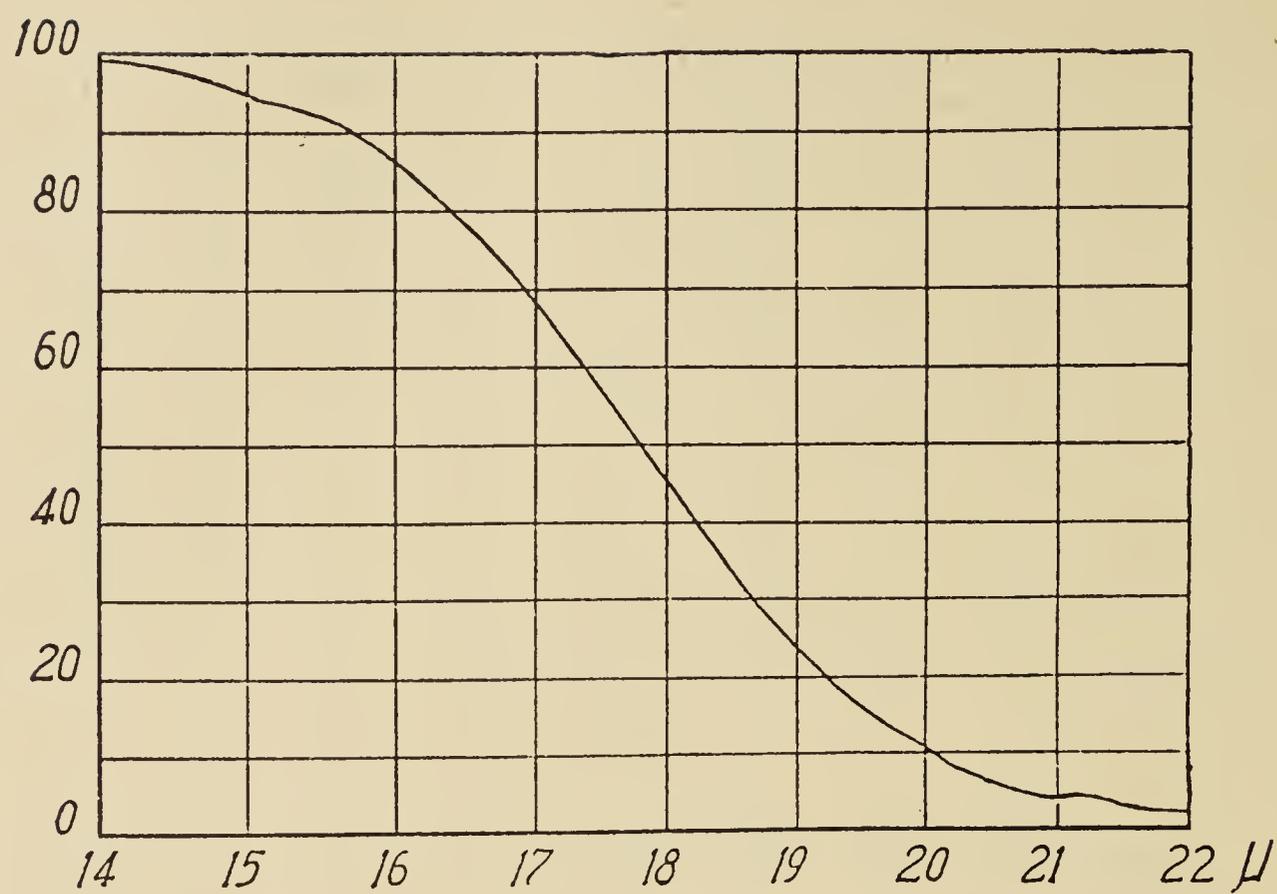


Figure 6. Infra-red absorption by rock-salt: 0.8 cm.

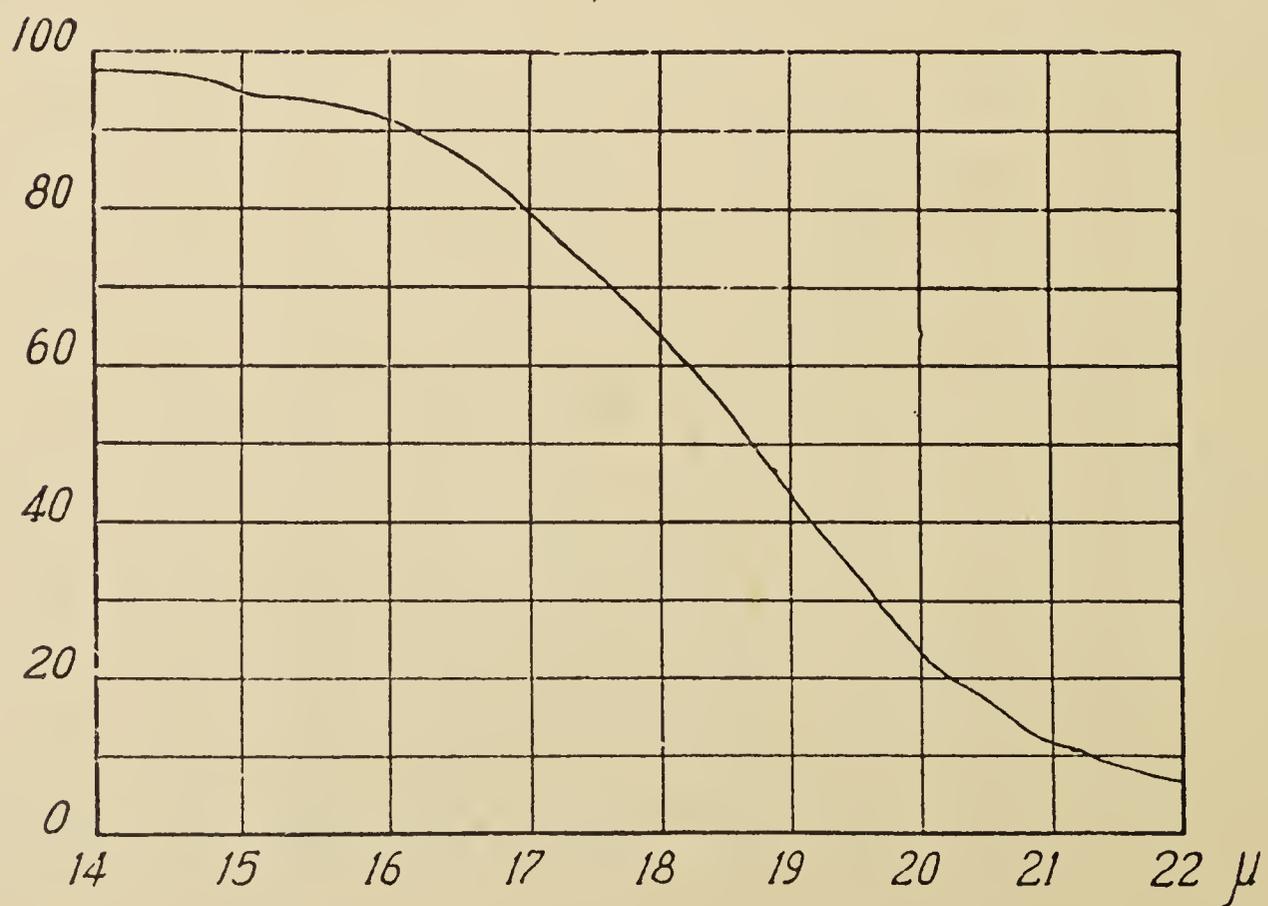


Figure 7. Infra-red absorption by rock-salt: 0.4 cm.

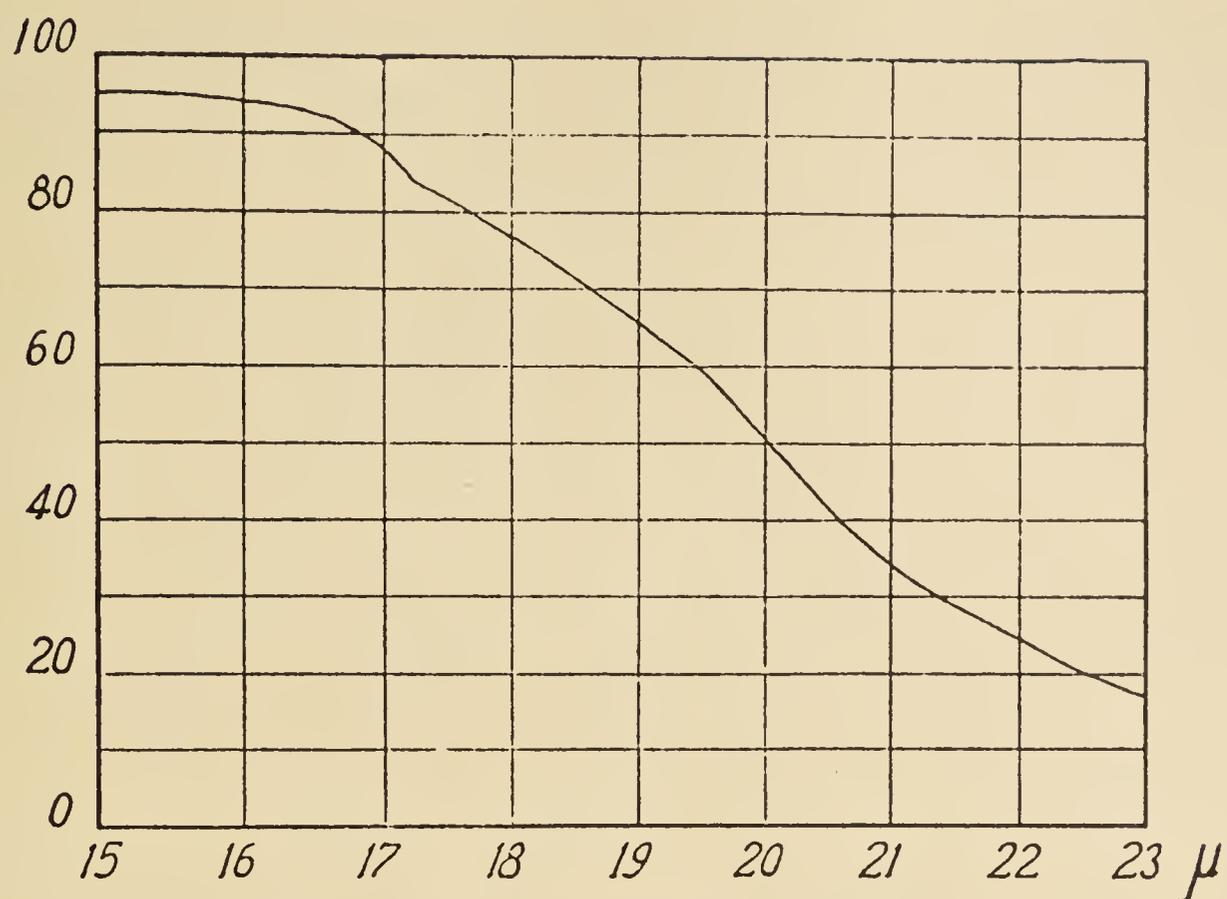


Figure 8. Infra-red absorption by rock-salt: 0.25 cm.

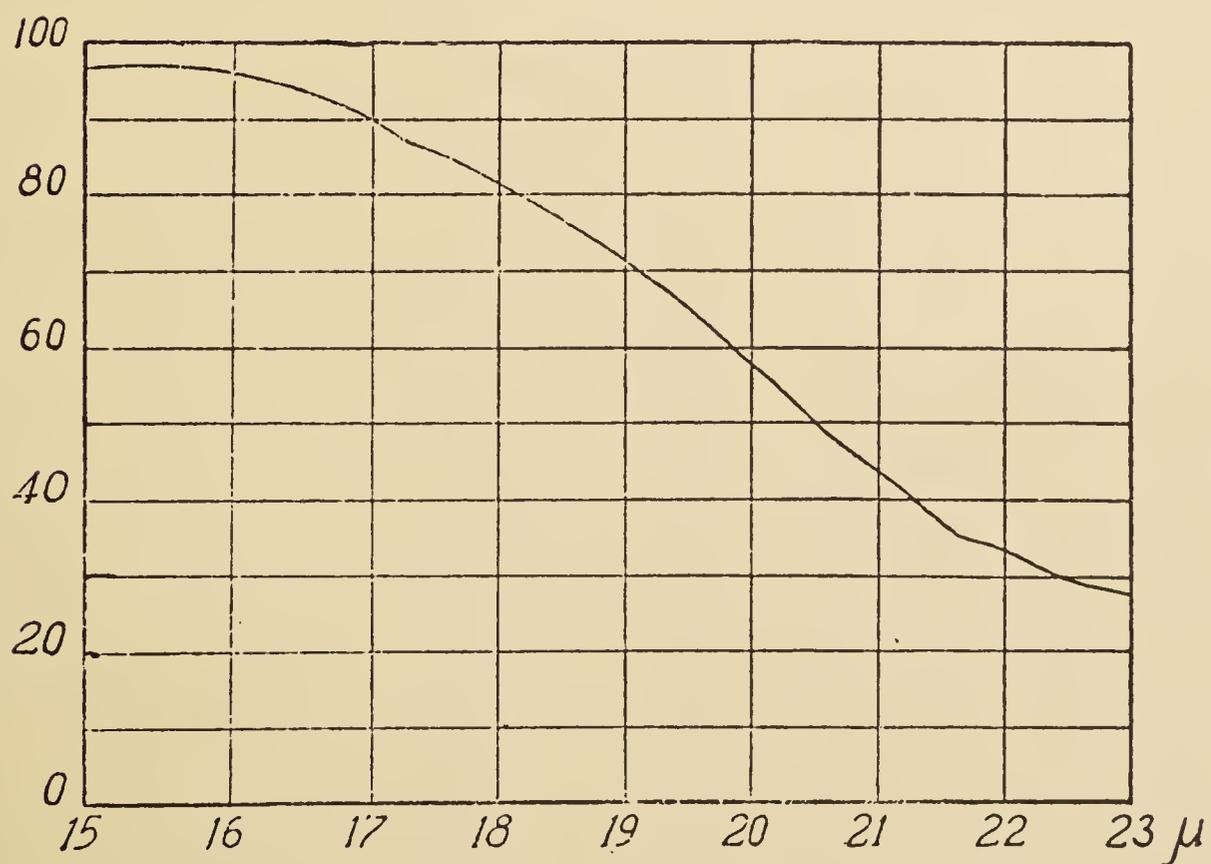


Figure 9. Infra-red absorption by rock-salt: 0.15 cm.

respectively for plates of thickness 8 mm, 4 mm, 2.5 mm and 1.5 mm. The cut-off in the region of the longer wavelengths has now disappeared and is replaced by a transmission which increases from 25% at $19\ \mu$ to 72% at the same wavelength as the thickness is diminished from 8 to 1.5 mm.

We may here draw attention to the remarkable fact that the percentage transmission curves are by no means always smooth graphs showing a progressive and continuous fall in transmission with increasing wavelength. Dips and sudden changes in direction are a noticeable feature. That they represent genuine features and not accidental faults in recording is shown by their appearance in the graphs for different thicknesses at the same wavelengths. It will suffice here to draw special attention to figure 8 which is the record for a plate 2.5 mm thick. The curve as reproduced commences with a 90% transmission at $15\ \mu$. This drops down rapidly and takes a sudden turn at $17.2\ \mu$. Another change in direction is noticeable at $19.5\ \mu$, still another at $20.7\ \mu$ and finally a small but distinct change in direction at $22\ \mu$.

6. Significance of the results

We shall now proceed to show that the experimental results set forth above and also the results of the published studies of Barnes and Czerny, and of Mentzel cited in the first part of this memoir find an intelligible explanation in the light of the theoretical considerations expounded earlier in this memoir. We shall commence by assuming that the frequencies of the five modes of coupled

Table 1. Vibration frequencies of rock-salt

	Mode	I Order	II Order	III Order	IV Order	V Order
I	cm^{-1}	180	360	540	720	900
	μ	55.6	27.8	18.5	13.9	11.1
II(a)	cm^{-1}	150	300	450	600	750
	μ	66.7	33.3	22.2	16.7	13.3
II(b)	cm^{-1}	129	258	387	516	645
	μ	77.5	38.8	25.8	19.4	15.5
II(c)	cm^{-1}	110	220	330	440	550
	μ	90.9	45.5	30.3	22.7	17.9
II(d)	cm^{-1}	92	184	276	368	460
	μ	109	54.5	36.2	27.2	21.7

oscillation of the Na and the Cl nuclei in rock-salt at room temperature are as shown below in table 1, both as wavelengths and as wave-numbers. The figures find their justification in the theoretical calculations presented in the first part of the memoir and corrected on the basis of the spectrographic data emerging from Rasetti's investigation. Table 1 also shows the overtones of the five frequencies up to and inclusive of the fifth order.

A scrutiny of the figures in table 1 enables us to understand the absorptive behaviour of rock-salt in the various ranges of frequency. In the wavelength range between $13\ \mu$ and $18\ \mu$, the absorptions that could manifest themselves are the fourth-order absorptions of modes I and II(*a*) and the fifth-order absorptions of modes II(*a*), II(*b*) and II(*c*). These would necessarily be very weak and would need large absorption paths to enable them to be observed. They would also disappear quickly when the path is diminished. In the wavelength range between $18\ \mu$ and $24\ \mu$ the third-order absorptions of modes I and II(*a*) would appear, supplemented by the fourth-order absorptions of modes II(*b*) and II(*c*) and the fifth-order absorptions of mode II(*d*). The strength of the third-order absorptions would naturally be far greater than those of higher orders appearing between $13\ \mu$ and $18\ \mu$. It is, therefore, not surprising that thicknesses which allow a notable transmission in that region are completely opaque to greater wavelengths.

The vibrations of the structure responsible for the absorptions of the third, fourth and fifth orders would necessarily be of large amplitude. In consequence, the vibrations excited would be a superposition of the various normal modes approximating to each other in frequency and not the individual modes by themselves. In these circumstances, we could scarcely expect to find any observable evidence of the discreteness of the normal modes. Nonetheless, some indications of it do appear. The remarkable features noticed in the absorption curve reproduced in figure 8 for a thickness of 2.5 mm may be cited as an example.

The absorptions of the second-order would be far more powerful than those of the third-order. Hence, much thinner layers, of the order of a hundred microns or less, would be needed to obtain any observable transmission in the region where the second-order absorptions operate. There is however much less crowding up of the normal modes. Hence it should be possible to find observational evidence of the discreteness of the absorption frequencies. The arrest in the absorption curve at about $34\ \mu$ noticed by Mentzel with rock-salt plates some 30 microns thick is clearly identifiable with the second-order absorption of mode II(*a*) listed in table 1. Likewise, the arrest extending from $40\ \mu$ to $44\ \mu$ and observed with plates 8 microns thick by Barnes and Czerny is clearly a superposition of the second-order absorptions of modes II(*b*) and II(*c*) shown in table 1.

Using evaporated films of NaCl only a few microns thick, Barnes and Czerny succeeded in obtaining an observable transmission in the spectral region where the infra-red activity is strongest and intense reflections appear. They studied the spectral character of the transmitted radiation for various thicknesses of the films

employed by them. The results which they reported, as also Czerny's observations on the variations of the reflecting power with wavelength, form a study in themselves. They are more appropriately discussed in a later part of this memoir.

Summary

Infra-red activity is shown to be a consequence of the periodic movements of the electron clouds in the crystal excited by the field of the incident radiation. The accompanying oscillations of the positively charged nuclei determine the frequencies but are not themselves the cause of the activity.

It is shown that of the nine modes of free vibration of the rock-salt structure, the mode of highest frequency is intensely active both in the first and the higher orders. Four other modes are inactive in the first-order but active in higher orders. The remaining four are totally inactive. Spectrographic records of the absorption of rock-salt over a wide range of thicknesses are presented and explained in terms of the activity of these modes. The results reported by Mentzel and by Barnes and Czerny on the transmission spectra of rock-salt are explained on the same basis.

The spectroscopic behaviour of rock-salt and the evaluation of its specific heat—Part III. The spectrum of light-scattering

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1. Introduction

In the first part of this memoir, the modes of free vibration characteristic of the structure of rock-salt were described and it was shown how their frequencies could be computed. In the second part of the memoir, the activities of these modes in the absorption and reflection of infra-red radiation were discussed. Experimental data were presented which showed clearly that the normal mode of highest frequency is active not only as a fundamental but also as overtones of higher orders. The observed infra-red behaviour of rock-salt over a wide range of frequencies of the incident radiation was discussed and explained in terms of the activities of its characteristic modes of vibration.

The present part of the memoir is concerned with an entirely different spectroscopic technique which enables the existence of the discrete normal modes of vibration to be established and their frequencies as theoretically evaluated to be checked by comparison with the results of experiment. This technique makes use of the frequency shifts observed when monochromatic light traversing the crystal emerges after diffusion in its interior and the diffused radiation is examined spectroscopically. The intensity of the radiation so diffused is a very small fraction of that traversing the crystal. But this very circumstance makes the procedure one of the highest value for the purposes in view. For, the complications which are inherent in the use of infra-red radiation in the study of the spectroscopic behaviour of such an intensely absorbing material as rock-salt are entirely avoided. The spectroscopic picture of the crystal which emerges from the recorded spectra of the diffused light is very simple, clear and definite.

We shall begin with a few remarks of a general nature. The study of the diffusion of monochromatic light by the molecules of diatomic gases, e.g., oxygen and nitrogen, gives us an insight into the origin of the frequency shifts in light-scattering. These shifts are readily identifiable with the characteristic vibrational frequencies of the molecules. The appearance of scattered radiations of altered

wavelength is thus explicable as a consequence of a periodic variation in the power of the molecule to scatter light resulting from the relative movements of its atoms in such vibration. A similar explanation can be given for the frequency shifts observed in the diffusion of light by crystals, the structural units in the crystal instead of the molecules of the gas being regarded as the vibrating systems. The structural units in a crystal are held to fixed positions and cannot move freely in the manner of the molecules in a gas. This circumstance has necessarily to be taken into account in considering the dynamics of their vibrations. But in respect of the frequency shifts arising from their internal vibrations, the randomness of phase of the scattered radiations renders the situation not essentially different from that of scattering by the individual molecules of a gas.

2. Scattering of light with doubled frequency shifts

As has been remarked above, the frequency shifts observed in the scattering of light may usually be identified with the vibrational frequencies of the scattering units. There is however a remarkable class of cases in which spectral shifts are observed having double the frequency of the vibrational modes which give rise to them. We may as an illustration mention the facts emerging from a study of the scattering of light in calcite. The CO_3 groups in that crystal have four internal modes of vibration. Three of them give frequency shifts of 712 cm^{-1} , 1086 cm^{-1} and 1436 cm^{-1} which may be identified respectively with the frequencies of three possible modes of vibration of the CO_3 group in its own plane. We are here concerned with a fourth frequency shift of 1749 cm^{-1} which is recorded with an intensity about equal to that of the 1436 cm^{-1} shift.

Now, the fourth mode of vibration of the CO_3 group is an out-of-plane movement in which the C atom oscillates along a line perpendicular to the O_3 group and finds itself alternately above and below the plane of the group. Such an oscillation may be expected to be strongly active in the absorption of infra-red radiation. Actually, a well-defined peak appears in the infra-red absorption spectrum of calcite at about 874 cm^{-1} and this is identified as arising from just such a vibration. But no line having that frequency shift or anywhere near it is recorded in the spectrum of the scattered light. We are thus obliged to infer that the frequency shift of 1749 cm^{-1} arises from the infra-red active vibrational mode but is recorded in the scattering of light with double its frequency.

A doubling of the frequency shift in light-scattering as compared with an infra-red absorption frequency may be explained in the following manner. The infra-red activity arises from the movements of the electron clouds in the crystal. These movements have necessarily the same frequency as the movements of the atomic nuclei. In the scattering of light, however, we are concerned with the optical polarisability of the entire electronic cloud and this depends on its geometric configuration. In the particular case of the CO_3 group in calcite it is clear that the

configuration of the group takes the same form twice in each oscillation. The periodic variation of optical polarisability has therefore twice the frequency of the vibration and hence the resulting frequency shift is also doubled. What is specially remarkable is that its intensity is comparable with those of the frequency shifts of the ordinary kind due to the other modes of vibration and that it is far greater than the intensity with which a shift of 2173 cm^{-1} (double that of the planar oscillation of 1086 cm^{-1}) is recorded in the spectrum.

3. The rock-salt spectrum

We proceed to show that an effect of the same general nature as that considered and explained above in the case of calcite is exhibited by all the nine normal modes of vibration of the rock-salt structure. We may begin by considering the triply degenerate mode of highest frequency which is highly active in the absorption of infra-red radiation. In this mode the sodium and chlorine nuclei with their associated electronic clouds move in opposite phases with amplitudes inversely proportional to their masses. *Twice* in each oscillation, a chlorine nucleus comes closest to a sodium nucleus either from one side or from the other. In such an approach, the power of the NaCl group to scatter light is notably increased beyond what it is when the Na and Cl nuclei are separated by their normal spacing in the crystal. Accordingly, the periodic variations of the scattering power of the NaCl groups in the crystal have *twice* the frequency of the vibrational mode. The frequency shift to which it gives rise is therefore also of double frequency. A component having the same frequency as the vibrational mode is totally absent, since the approach of a chlorine nucleus to a sodium nucleus is balanced by the recession of a chlorine nucleus from the same sodium nucleus on the opposite side. In other words, the vibrational mode is antisymmetric with respect to each sodium nucleus and each chlorine nucleus in the assembly. It is therefore inactive in light-scattering in the sense of the term as ordinarily understood.

The same argument may be extended to the four other coupled oscillations of the Na and Cl nuclei. Two of these modes are tangential and the two others normal to the cubic layers in the crystal; in all these cases, the movements in alternate layers are in opposite phases. In the tangential mode designated in the earlier parts of this memoir as II(*a*), the Na and Cl nuclei approach and recede from each other in much the same manner as in the mode I discussed above. The alternation in phase from layer to layer leaves the argument unaffected; for, at the instant when the Cl and Na nuclei are closest to each other in one layer, they would also be closest to each other in the next layer. It follows that mode II(*a*) would be active in the double-frequency modified scattering of light to much the same extent as the principal mode already considered. Indeed, mode II(*a*) having

a degeneracy of six may be expected to exhibit a greater intensity than mode I which is only triply degenerate.

Considering next the tangential mode designated as II(*d*) in which the Na and Cl nuclei in each cubic layer oscillate in the same phase, the phases of the movements being reversed in the successive layers, it is evident that the double-frequency effect would also arise in respect of this mode but it would be very much feebler. For, the movements of the Na and the Cl nuclei being in the same phase, their approaches to each other would necessarily be much less close than when the movements are in opposite phases. The periodic fluctuations in the scattering power of the NaCl groups would therefore be relatively small and hence the observable effect of mode II(*d*) as recorded in the spectra of the scattered light should be far less conspicuous.

Arguments of the same kind may be extended to the consideration of the activity of the triply degenerate oscillations of the Na and Cl nuclei normal to the cubic planes designated as modes II(*b*) and II(*c*) respectively. In mode II(*b*) the Na and Cl nuclei move in the same phase and this has the higher frequency, while II(*c*) in which they move in opposite phases has the lower frequency. But the approaches between the Cl and Na nuclei which give rise to an increased scattering power are those between the nuclei which are in adjacent layers. Hence, it follows that the mode II(*b*) of the higher frequency would be much more strongly active than mode II(*c*) of the lower frequency. Since both the modes are only three-fold degenerate, their recorded intensities would be low. In particular, the mode II(*c*) of lower frequency would be recorded only very feebly.

4. Activity of the octahedral modes

We now proceed to discuss the activity of the modes in which the Na nuclei alone, or the Cl nuclei alone oscillate. The layers containing them are the octahedral planes of the crystal and the movement is either perpendicular or parallel to those planes, its phase being reversed in the successive layers. The oscillations perpendicular to the octahedral planes have a degeneracy of four and the nuclei move along the body-diagonals of the cube. The oscillations tangential to those planes have a degeneracy of eight and the nuclei move along one or another of the two-face diagonals appearing in the octahedral planes.

We proceed to consider the nature of the movements in these modes. In the perpendicular modes, a nucleus would approach its three nearest neighbours on the one side and recede from its three nearest neighbours on the other side. In the parallel modes, a nucleus would approach two of its nearest neighbours on one side and recede from two of its nearest neighbours on the other side. In either case, the movements would not give rise to frequency-shifts in light-scattering of the usual kind. They would, however, all be active in the modified scattering of double frequency. The parallel movements, being twice as numerous, may be

expected to be recorded with greater intensity than the perpendicular ones.

We may summarise the overall picture which emerges from the foregoing considerations regarding the spectroscopic behaviour of rock-salt in light-scattering as follows:

- (a) All the nine normal modes would exhibit a doubled frequency shift but with very different intensities.
- (b) The triply degenerate mode of highest frequency would be strongly recorded but would be inferior in intensity to the cubic mode of lower frequency similar to it in character but which is six-fold degenerate.
- (c) The two cubic modes of low frequency would be recorded only feebly, the one which is three-fold degenerate even more weakly than the other of lowest frequency which is six-fold degenerate.
- (d) The eight-fold degenerate oscillation of the chlorine nuclei tangential to the octahedral planes should appear with notable intensity as a conspicuous feature in the spectrum, being adjacent to the two feebly recorded modes of lowest frequency.
- (e) The eight-fold degenerate oscillation of the sodium nuclei parallel to the octahedral planes would be recorded more strongly than the four-fold degenerate movement perpendicular to those planes.

5. The spectrum of light scattering

The vibration frequencies of the five cubic modes involving coupled oscillations of the Na and the Cl nuclei were listed in an earlier part of this memoir. To this list we must now add the frequencies of the four octahedral modes in which only the Na or only the Cl nuclei oscillate. As a rough approximation, the frequencies of these modes can be expressed in terms of the infra-red active mode of highest frequency by replacing the reduced mass of the two nuclei in its formula by the mass of the Na nucleus alone or of the Cl nucleus alone. But, as already remarked upon and explained in the first part of the memoir, the values thus obtained need correction and their frequencies have to be increased by amounts which are greater for the perpendicular vibrations than for the parallel ones. The corrected frequencies are most conveniently determined from the spectral shifts observed in light-scattering, as they are readily identified in those spectra.

Table 1 gives the frequencies of all the nine normal modes. Their degeneracies and descriptions are also shown. They have been entered in table 1 in the descending order of frequency. The doubled frequency shifts in light-scattering appear in the penultimate column. The entry against each frequency shift under the head intensity is based on the indications of theory, viz., the degeneracy of the mode and the nature of the movements involved. These considerations have already been discussed in detail above and need not therefore be repeated here.

Table 1. Modes and frequencies (cm^{-1})

Modes	Degene- racy	Principal mode	Cubic class	Octahedral class	Doubled frequency	Intensity
I	3	180 (NaCl)	—	—	360	Moderate
III(a)	4	—	—	170 (Na)	340	Moderate
III(b)	8	—	—	157 (Na)	314	Strong
II(a)	6	—	150 (NaCl)	—	300	Strong
III(c)	4	—	—	140 (Cl)	280	Strong
II(b)	3	—	129 (NaCl)	—	258	Weak
III(d)	8	—	—	117.5 (Cl)	235	Intense
II(c)	3	—	110 (NaCl)	—	220	Very weak
II(d)	6	—	92 (NaCl)	—	184	Weak

6. The consequences of thermal agitation

It is a familiar experience in studies on the scattering of light in crystals to find that the observed frequency shifts exhibit a thermal effect. The lines sharpen and the frequency shifts show a readily measurable increase when the crystal is cooled down to liquid air temperature. When, on the other hand, the crystal is warmed up, the lines become more diffuse as the result of an asymmetrical broadening. As a consequence of such broadening, the frequency shifts also diminish. The effects of this nature are both absolutely and relatively more conspicuous in the case of the vibrational modes of low frequencies. As examples may be mentioned the behaviour of calcite and of quartz in which they have been very fully studied. A thermal broadening and the accompanying diminution of the frequency shifts would necessarily occur also in the case of rock-salt. Since we are concerned with double-frequency scattering, they would be magnified two-fold. On the basis of the known data for quartz and calcite we may expect a broadening of the lines in the spectrum of rock-salt of about ten wave-numbers.

It follows from what has been stated that in the crowded spectrum indicated by the figures in table 1, the thermal broadening would result in the resolution of the frequency-shifts which are not very different becoming distinctly imperfect. When, however, a strongly recorded frequency shift has only weak companions on either side, its character as a discrete line-shift would be more clearly apparent.

7. Comparison with the experimental results

With a crystal of rock-salt five centimetres thick which was illuminated by the extremely intense ultra-violet radiation at $\lambda 2536.5$ emitted by a water-cooled magnet-controlled mercury arc in quartz and giving an exposure of 8 hours,

Rasetti obtained a remarkable spectrogram. This was published with a microphotometer record of the spectrum alongside of it. An enlargement of this microphotometer curve copied directly from Rasetti's original publication is reproduced below as figure 1 in the text.

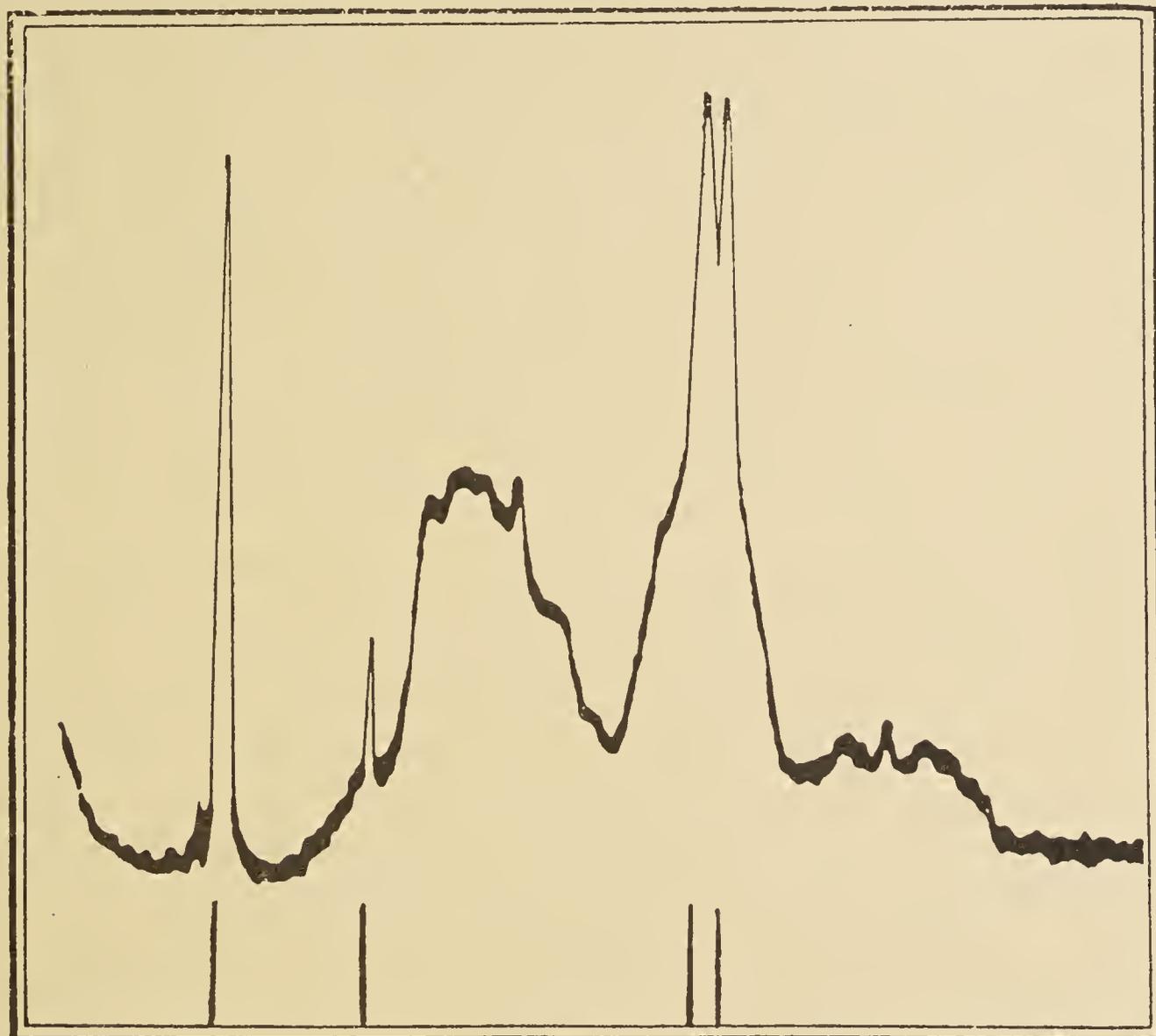


Figure 1. Microphotometer record (after Rasetti).

A special method was employed by Rasetti to prevent the complete fogging of the photographic plate which would have otherwise resulted from such prolonged exposure to intense illumination. A filter of mercury vapour was introduced which absorbed the 2536.5 radiation entering the instrument before it reached the photographic plate. A remarkably clear and well-exposed spectrogram was thus obtained. Neither the accompanying $\lambda 2535$ radiation nor the faint continuum extending to about 50 wave-numbers on either side of $\lambda 2536.5$ is cut out by the filter. They are recorded on the spectrogram, but have no significance.

The frequency shifts which arise from the scattering of the 2536.5 radiation in rock-salt are all found to lie between the limits 360 cm^{-1} and 184 cm^{-1} indicated by the theory. Beyond these limits, the spectrum falls off steeply in intensity. The fall on both sides would have been even steeper had the inevitable background of

continuous spectrum which is an accompaniment of the monochromatic radiations of the mercury arc been totally absent in the record. But such absence could scarcely have been hoped for in view of the prolonged exposures necessary to obtain the spectrum.

For the convenience of the reader, the original spectrogram of rock-salt has been reproduced in a somewhat enlarged form as figure 1 in plate I accompanying the present memoir. On an inspection of the spectrum, it is evident that it presents precisely those features which would result from the nine double-frequency shifts listed in table 1 being recorded in the positions and with the relative intensities listed in table 1. On closer examination, it becomes clear that the correspondence between the observed spectrum and the theoretical conclusions listed in table 1 extends to all the observable details in it. The experimental conditions, viz., the small dispersion of the spectrograph and the broadening of the frequency-shifts by the thermal agitation in the crystal are unfavourable to a complete resolution of the nine frequency shifts from each other. Nevertheless, it is clear that they are all present and have the positions and relative intensities indicated by the theory.

We may begin by referring to a striking feature in the spectrogram, viz., the well-defined frequency shift of 235 cm^{-1} which stands out in the record on both sides of the exciting radiation. The shift appears in a part of the spectrum where the frequency shifts on either side are weak or very weak as indicated by the theory and also as actually observed. Naturally, therefore, the 235 cm^{-1} frequency shift is permitted to exhibit its true character as a discrete line-shift. It is not surprising also that the intensity of the shift due to the eight-fold degeneracy of the vibration makes it a prominent feature in the spectrum.

The two lowest frequencies listed in table 1 are coupled oscillations of the Na and the Cl nuclei in the cubic planes. The theory indicates that they would appear in the spectrum with a much lower order of intensity than the other modes, the reason being the Na and Cl nuclei have the same phase of vibration and cannot therefore make close approaches to each other. The two modes should also differ in their relative intensities by reason of the degeneracies being different, being three and six respectively. These consequences of the theory are in striking accord with the experimental facts. Actually, the frequency shifts of 220 cm^{-1} and 184 cm^{-1} are by far the feeblest recorded in the spectrum. The shift of 220 cm^{-1} is, in particular, so weak as scarcely to be visible in the reproduction of the spectrum. Its presence in the microphotometer record can be made out with some difficulty being obscured by the steep rise in the intensity as we approach the intense 235 cm^{-1} shift. The shift of 220 cm^{-1} can, however, be readily recognised in the microphotometer record on the "anti-stokes" side of the spectrum as a second and weaker hump between the 184 cm^{-1} and 235 cm^{-1} shifts (figure 1 in the text, right-hand side of the microphotometer curve.)

It is a significant consequence of the theory that the smaller frequency shift of 300 cm^{-1} should be recorded with twice the intensity of the larger shift of 360 cm^{-1}

by reason of its higher degeneracy, though the oscillations are very similar to each other in character. That this is actually the case is clear from the spectrogram itself. In the microphotometer record (figure 1 in the text, left-hand side of the curve), the frequency shift of 300 cm^{-1} stands at a much higher level than 360 cm^{-1} . It is well known, however, that differences in intensity between the different lines in a spectrogram are better appreciated when the exposure is not very heavy, as the photographic blackening is then not too great to show up the gradations in exposure. Likewise, for a microphotometer record, a moderately exposed plate is more suitable than a heavily exposed one. For, in the latter case, the differences of intensity are greater reduced in the transmission through the blackened plate which is recorded photometrically.

The importance of the foregoing remarks will be realised on an examination of the microphotometer record reproduced above in the text as figure 1. Rasetti's spectrogram and its microphotometer trace show the spectral shifts recorded on both sides of the exciting radiation $\lambda 2536.6$. On the "anti-stokes" side, the exposures are much less heavy and hence its microphotometric record is better suited to exhibit the relations of intensity between adjacent parts of the spectrum than the record of the more heavily exposed spectrum on the other side.

It has been already remarked that the 220 cm^{-1} shift which is only vaguely indicated on the heavily exposed side of the record is quite clearly seen on the "anti-stokes" side. Likewise, all the frequency shifts listed in table 1 are clearly visible on the "anti-stokes" side of the microphotometer record distinctly separated from each other. Instead of the 360 cm^{-1} and 340 cm^{-1} shifts appearing fused into a single band as on the heavily exposed side, they are seen on the "anti-stokes" side quite clearly as two distinct steps one above the other. The third step which is visible in the record is the 314 cm^{-1} shift. Two other strongly recorded shifts, viz., 300 cm^{-1} and 280 cm^{-1} , are seen higher up in the photometer curve. The weak 258 cm^{-1} shift appears as the drop in intensity which immediately precedes the strongly recorded peak shift of 235 cm^{-1} . Thus, the microphotometer record on the "anti-stokes" side enables us to recognise all the nine frequency shifts individually and to appreciate the great differences in intensity which they present more clearly than the record on the heavily exposed side permits.

We may sum up the foregoing by stating that the experimental results completely establish the correctness of our theoretical approach and are a verification of the various observable consequences to which the theory points.

8. Summary

All the nine normal vibrational modes of the rock-salt structure can give frequency shifts in light-scattering which are twice their respective frequencies but are of very different intensities, determined by their degeneracies and the nature of

the movements of the Na and Cl nuclei in those modes. The doubled frequencies in cm^{-1} with their respective degeneracies are 360(3), 340(4), 314(8), 300(6), 280(4), 258(3), 235(8), 220(3), 184(6). The spectroscopic facts are in full agreement with the theoretical deductions.

Appendix

Reflection and transmission of long waves

The frequencies of the characteristic vibrational modes of the rock-salt structure determined spectroscopically and expressed as infra-red wavelengths are the following: 55.6μ , 58.8μ , 63.7μ , 66.7μ , 71.4μ , 77.5μ , 85.0μ , 90.9μ and 108μ . The question arises of the part they play in the reflection by rock-salt surfaces and in the transmission through thin films of long-wave infra-red radiation.

Amongst these modes, that of the highest frequency with the characteristic wavelength 55.6μ stands in a class apart by itself, being the strongly infra-red active fundamental. It is therefore to be expected that this mode would play a dominating role in the reflection of infra-red radiation and that it would also manifest itself as the principal cause of absorption in thin films.

The reflecting power of rock-salt actually reaches its maximum value of about 90% at a wavelength which is nearly the same as that of its active fundamental. But it is considerable both at shorter and at longer wavelengths. On the long wavelength side, the reflecting power diminishes progressively and reaches a limiting value of 20% at and beyond 100μ . On the short wavelength side, the reflecting power drops off more quickly and becomes quite small at about 33μ . There are indications of a minor maximum of reflecting power at about 38μ .

That the reflecting power at shorter wavelengths is considerable is readily explained. Four of the characteristic vibrational modes are coupled oscillations of the Na and the Cl nuclei in the crystal which are strongly infra-red active with a *doubled frequency*. The absorption wavelengths thus arising are 33.3μ , 38.8μ , 45.5μ and 54.3μ respectively. The existence of absorptions at these wavelengths is indeed demonstrable by observations with rock-salt plates with appropriately chosen thicknesses. Their co-operation with the active fundamental in infra-red reflection is a natural consequence. That the reflecting power becomes negligible at wavelengths less than 33μ is only to be expected in these circumstances.

The existence of a whole series of normal modes of vibrations of the rock-salt structure with characteristic wavelengths ranging between 55μ and 108μ furnishes us with a clue to the explanation of the fact that the reflecting power of rock-salt diminishes only slowly in this range and reaches its limiting value of 20% beyond 100μ . Infra-red activity arises from the movements of the electronic clouds in the crystal set up by the incident radiation. A complete independence of the normal modes of vibration and of their excitation cannot be assumed in these

circumstances. That the different normal modes would co-operate to varying extents and that such excitation would manifest itself in the reflecting power of the crystal is only to be expected.

In determining the transmission by the thinnest films of NaCl, the fundamental absorption at 55.6μ would naturally play the leading role. But one cannot ignore the existence of other absorptions which would simultaneously operate. Amongst these are the modes which are active with doubled frequencies as stated above. We should also take account of the whole series of modes with greater wavelengths which may be simultaneously excited by the reason of the non-independence of normal modes. It would not be surprising if in these circumstances the wavelength of maximum absorption is shifted appreciably towards wavelengths greater than 55.6μ .

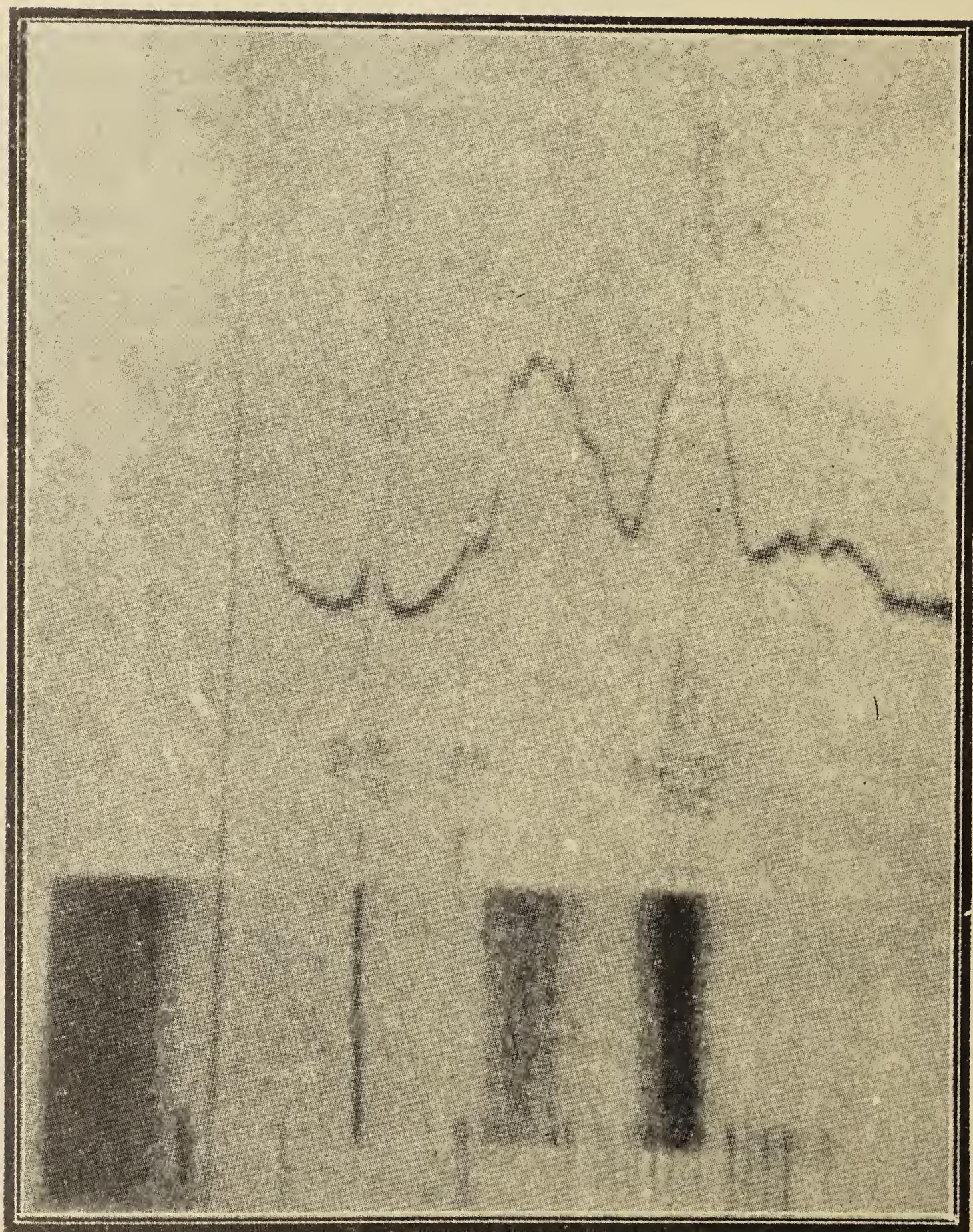


Figure 1. Double-frequency shifts in light-scattering by rock-salt.

Plate I

The spectroscopic behaviour of rock-salt and the evaluation of its specific heat—Part IV. Specific heat and spectral frequencies

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1. Introduction

The numerous published measurements of the thermal energy-content of crystalline solids and its variation with temperature make it clear that the theory of specific heats is concerned with the movements of the atomic nuclei in crystals about their positions of equilibrium and especially with the frequencies of their vibrations. A clear picture of the nature of these vibrations emerges if we take the basic facts of crystal architecture as our starting point, viz., that a crystal consists of an immense number of similar and similarly situated units of structure. Each unit of structure contains a group of atomic nuclei which can interact with each other through the electrons which hold them together. The next step is to make use of the theory of small vibrations in classical mechanics to find the normal modes and frequencies of free vibration of these nuclei about their positions of equilibrium. In treating this problem, we have of necessity to recognise and take account of the three-dimensional periodicity of the crystal architecture. The principles of thermodynamics and of the quantum theory have then to be introduced and applied to the problem. They indicate that the normal modes deduced classically would be excited to various levels of energy, the relative probabilities of such excitation being determined by the respective energies and the absolute temperature. The average energy associated with each such normal mode and hence also the total average energy of all the normal modes taken together can then be computed. A multiplication of this average by the number of the oscillators in the crystal considered gives the total thermal energy of the solid as a function of the temperature.

It has been shown in the preceding parts of this memoir that a basically similar approach enables us to explain or elucidate the spectroscopic properties of the crystal. It follows that the thermal and spectroscopic behaviours of the crystal stand in the closest relationship to each other. It should therefore be possible by

making use of the spectroscopically determined frequencies of vibration to evaluate the specific heat of the crystal as a function of temperature and proceed to a comparison of the results thus obtained with the measured specific heats. No data are required for such an evaluation except those emerging from the spectroscopic studies. It follows that an agreement between theory and experiment would constitute a perfect demonstration of the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.

2. The spectral frequencies of rock-salt

In the case of magnesium oxide which has been dealt with in memoir No. 127 appearing in the same issue of these *Proceedings*, the spectroscopic frequencies were determined by the study of infra-red absorption in that crystal. In the case of rock-salt now considered, we have two distinct methods of investigation available which, as has already been noticed, give results supporting each other and confirming the inferences from theory. Of the two methods of study, viz.,

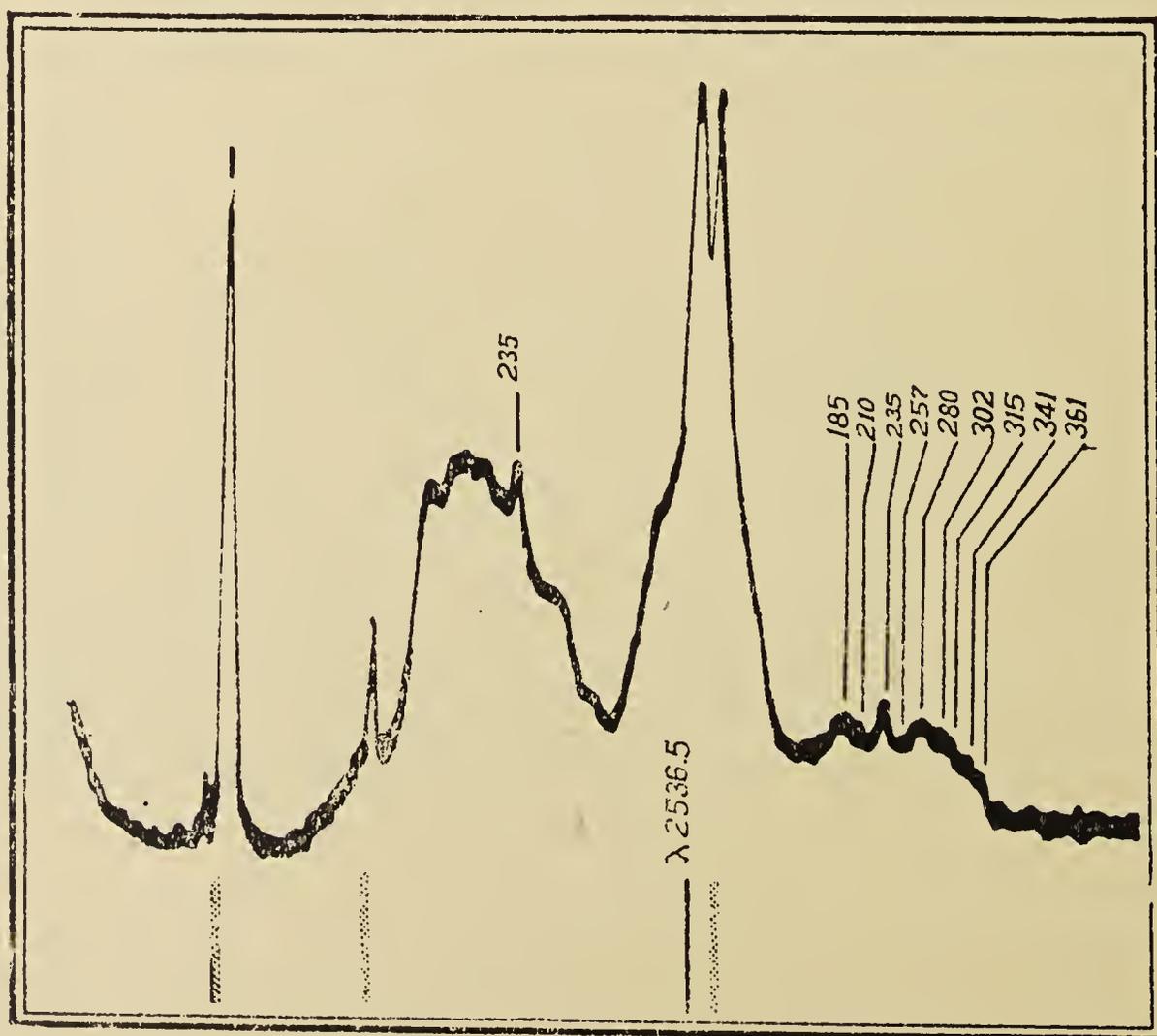


Figure 1. Microphotometer record showing frequency shifts.

infra-red spectroscopy and the scattering of light, the latter is definitely superior, since the data furnished by it are both complete and exact. All the nine modes appear in light-scattering with doubled frequency shifts with respect to the position in the spectrum of the $\lambda 2536.5$ radiation of the mercury arc used to illuminate the crystal. The spectral shifts are recorded on both sides of the exciting radiation, and the microphotometer records of the spectrum on the two sides usefully supplement each other. On the heavily exposed side, the background due to the continuous radiation in the incident light is relatively less important, and the record therefore gives a truer picture of the spectrum taken as a whole. But, on the other hand, the heavy exposure results in obscuring finer detail and its microphotometer record fails to exhibit a complete resolution of the spectrum into its distinct components. The microphotometric record of the weakly exposed side is greatly superior in this respect. Not only does it reveal the nine distinct double-frequency shifts in the scattered light but also enables them to be read off directly from the record with tolerable accuracy.

Figure 1 in the text is the same record as that reproduced as figure 1 in the previous part of the memoir. But now the frequency shifts have been entered and shown against the visible peaks in the record which enabled them to be measured with reference to the position of the exciting radiation, the prominent 235 cm^{-1} shift being used to furnish the necessary scale of frequencies. The frequency shifts determined in this manner and entered in the figure differ little from those obtained by measurements under a micrometer of original spectrum plates recorded with rock-salt.

3. Comparison with the specific heat data

The manner in which we proceed from the spectroscopic frequencies to evaluate the specific heat of rock-salt as a function of the temperature is entirely analogous to that already fully explained for the case of MgO in a memoir appearing in the same issue of these *Proceedings*. It is unnecessary to traverse the ground here once again and it suffices to present a tabulation of the contributions to the specific heat made by the different normal modes of vibration, as also by the residual spectrum of vibration frequencies which is continuous and extends towards zero frequency. The normal frequencies of vibration made use of in the calculations are one-half the frequency shifts (in cm^{-1}) observed in the scattering of light.

Though the structure of rock-salt is similar to that of MgO, the two cases differ in certain important respects. The vibration spectrum of rock-salt lies much further out in the infra-red than that of MgO. As is to be expected in the circumstances, the increase in its specific heat from very low to normal values takes place for the most part in the region of liquid air and liquid hydrogen temperatures. Tabulations are therefore required in the case of rock-salt only for temperatures between 0 and 300 degrees absolute.

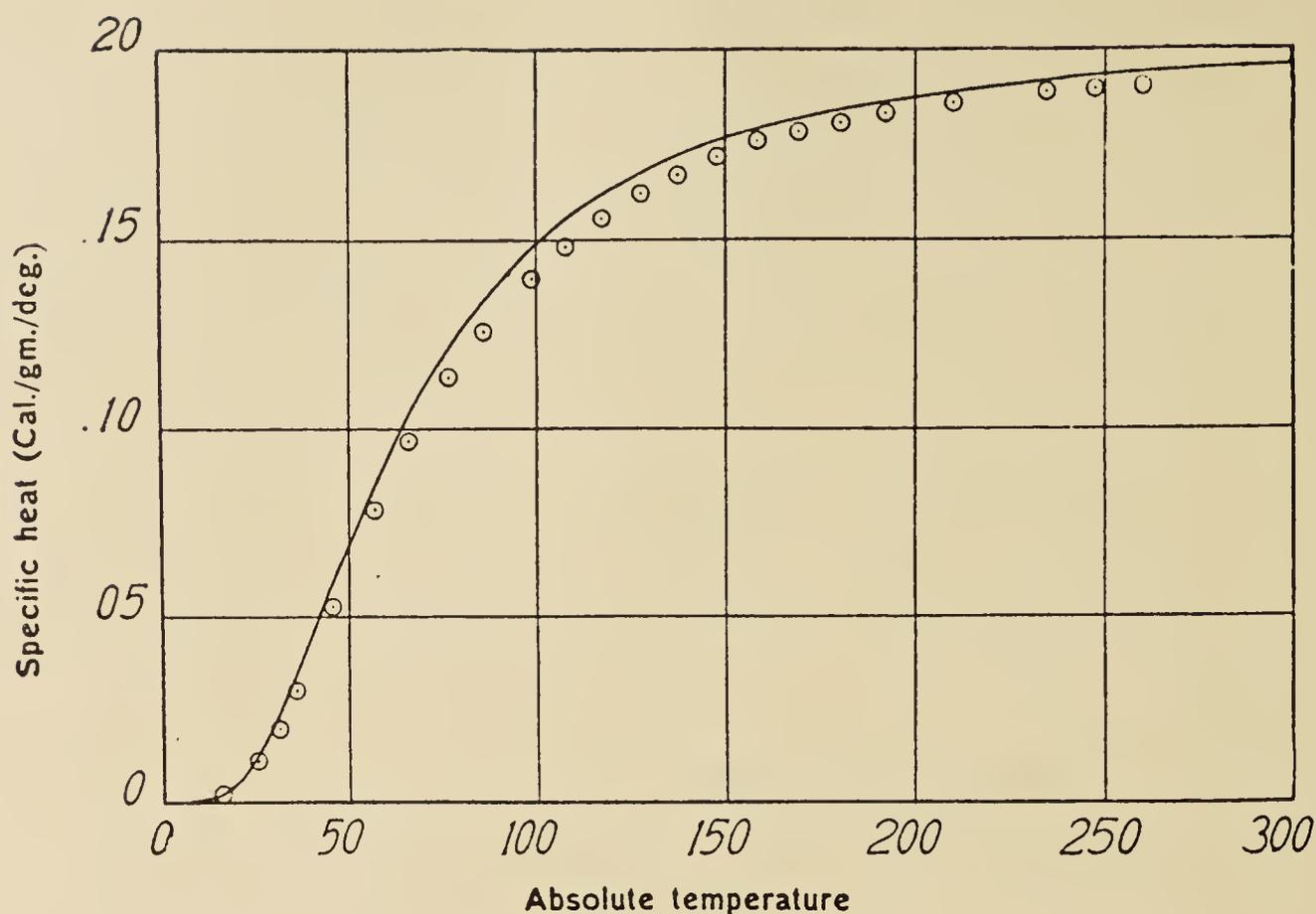


Figure 2. Comparison of theory and experiment. Theory———. Experiment $\odot \odot \odot$.

The foregoing remarks have some further implications. As has been pointed out in the third part of this memoir, the frequency shifts observed in light scattering exhibit a temperature effect. The frequency shifts broaden asymmetrically and also move to smaller values as the temperature is raised. In the case of rock-salt, the spectroscopic data we make use of were obtained with the crystal held at room temperature. Hence, it cannot be expected that these data would fit the specific heat curve at very low temperatures and especially at the temperatures where the specific heat changes most rapidly. We could only expect the theoretically calculated specific heats for low temperatures to agree with observed specific heats if the frequencies used had been determined with the crystal held at the same temperatures.

The foregoing remarks find support in the results of the actual computations. Tables 1 and 2 show the specific heats as computed and the results have been drawn as a continuous graph in figure 2 in the text. The experimental values in the same range of temperatures are given in table 5 and have been shown as dotted circles in figure 2. It will be seen that the experimental values lie systematically below the theoretical curve, the deviations being greatest in the range between 50 and 150 degrees absolute.

The differences between theory and experiment indicated in figure 2 arise, without doubt, by reason of the spectroscopic frequencies used in the calculations being less than the actual spectroscopic frequencies at low temperatures. Precisely what the latter are cannot be stated on the basis of present knowledge.

Table 1. Computation of the specific heats

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
3E ₁ (180 cm ⁻¹)	—	—	0.0023	0.1088	0.2929	0.4312	0.5223
4E ₂ (170 cm ⁻¹)	—	—	0.0047	0.1738	0.4278	0.6091	0.7235
8E ₃ (157 cm ⁻¹)	—	0.0001	0.0176	0.4359	0.9638	1.3059	1.5135
6E ₄ (150 cm ⁻¹)	—	0.0001	0.0181	0.3673	0.7652	1.0137	1.1610
4E ₅ (140 cm ⁻¹)	—	0.0002	0.0188	0.2876	0.5545	0.7099	0.7994
3E ₆ (129 cm ⁻¹)	—	0.0004	0.0226	0.2571	0.4517	0.5593	0.6180
8E ₇ (118 cm ⁻¹)	—	0.0026	0.0960	0.8042	1.3013	1.5608	1.6985
3E ₈ (110 cm ⁻¹)	—	0.0019	0.0502	0.3362	0.5154	0.6043	0.6506
6E ₉ (92 cm ⁻¹)	0.0004	0.0156	0.2056	0.8453	1.1482	1.2852	1.3569
3D(92 cm ⁻¹)	0.0240	0.0767	0.2458	0.5332	0.6378	0.6818	0.7036
Molecular heat (cal/gm/deg)	0.0244	0.0976	0.6817	4.1494	7.0586	8.7612	9.7473
Specific heat (cal/gm/deg)	0.0004	0.0017	0.0117	0.0710	0.1208	0.1499	0.1668

Table 2. Computation of the specific heats

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
3E ₁ (180 cm ⁻¹)	0.5805	0.6195	0.6468	0.6647	0.6805	0.6909	0.6983
4E ₂ (170 cm ⁻¹)	0.7952	0.8416	0.8738	0.9005	0.9156	0.9283	0.9377
8E ₃ (157 cm ⁻¹)	1.6398	1.7249	1.7807	1.8229	1.8510	1.8753	1.8927
6E ₄ (150 cm ⁻¹)	1.2507	1.3084	1.3528	1.3776	1.3965	1.4125	1.4248
4E ₅ (140 cm ⁻¹)	0.8530	0.8863	0.9114	0.9269	0.9390	0.9487	0.9554
3E ₆ (129 cm ⁻¹)	0.6542	0.6774	0.6920	0.7023	0.7106	0.7166	0.7204
8E ₇ (118 cm ⁻¹)	1.7807	1.8340	1.8673	1.8903	1.9087	1.9211	1.9326
3E ₈ (110 cm ⁻¹)	0.6785	0.6941	0.7063	0.7141	0.7197	0.7241	0.7274
6E ₉ (92 cm ⁻¹)	1.3945	1.4178	1.4347	1.4455	1.4535	1.4599	1.4644
3D(92 cm ⁻¹)	0.7159	0.7229	0.7281	0.7314	0.7338	0.7357	0.7370
Molecular heat	10.3430	10.7269	10.9939	11.1762	11.3089	11.4131	11.4907
Specific heat (cal/gm/deg)	0.1770	0.1835	0.1881	0.1912	0.1935	0.1953	0.1966

Any attempt to fit theory and experiment by using assumed values for the frequencies might well be thought artificial and unsatisfactory. It appeared however useful to present a second set of computations in which all the frequencies made use of are raised uniformly by 5% of their respective values. Such an increase is certainly not greater than would be justified by a comparison with those cases, e.g., quartz and calcite, where the effect of using liquid air temperatures on the vibration frequencies has been quantitatively studied. The fresh computations on this basis have been shown in tables 3 and 4, and their

Table 3. Computation of the specific heats

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
3E ₁ (189 cm ⁻¹)	—	—	0.0015	0.0925	0.2678	0.4058	0.5034
4E ₂ (179 cm ⁻¹)	—	—	0.0031	0.1478	0.3944	0.5794	0.6986
8E ₃ (165 cm ⁻¹)	—	0.0001	0.0121	0.3804	0.8966	1.2504	1.4693
6E ₄ (158 cm ⁻¹)	—	0.0001	0.0125	0.3212	0.7165	0.9725	1.1318
4E ₅ (147 cm ⁻¹)	—	0.0001	0.0138	0.2576	0.5233	0.6872	0.7804
3E ₆ (135 cm ⁻¹)	—	0.0002	0.0175	0.2339	0.4312	0.5443	0.6073
8E ₇ (124 cm ⁻¹)	—	0.0017	0.0749	0.7360	1.2504	1.5223	1.6715
3E ₈ (116 cm ⁻¹)	—	0.0012	0.0392	0.3104	0.4949	0.5901	0.6412
6E ₉ (97 cm ⁻¹)	0.0002	0.0106	0.1674	0.7949	1.1153	1.2624	1.3416
3D(97 cm ⁻¹)	0.0204	0.0665	0.2213	0.5146	0.6270	0.6746	0.6991
Molecular heat	0.0206	0.0805	0.5633	3.7893	6.7174	8.4890	9.5442
Specific heat (cal/gm/deg)	0.0004	0.0014	0.0096	0.0648	0.1149	0.1452	0.1633

Table 4. Computation of the specific heats

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
3E ₁ (189 cm ⁻¹)	0.5659	0.6073	0.6370	0.6566	0.6754	0.6856	0.6941
4E ₂ (179 cm ⁻¹)	0.7761	0.8280	0.8625	0.8883	0.9087	0.9213	0.9323
8E ₃ (165 cm ⁻¹)	1.6113	1.6985	1.7603	1.8092	1.8397	1.8620	1.8833
6E ₄ (158 cm ⁻¹)	1.2268	1.2909	1.3355	1.3672	1.3883	1.4045	1.4178
4E ₅ (147 cm ⁻¹)	0.8397	0.8754	0.9046	0.9213	0.9337	0.9440	0.9522
3E ₆ (135 cm ⁻¹)	0.6468	0.6708	0.6878	0.6983	0.7071	0.7133	0.7181
8E ₇ (124 cm ⁻¹)	1.7572	1.8201	1.8567	1.8833	1.9020	1.9149	1.9273
3E ₈ (116 cm ⁻¹)	0.6708	0.6888	0.7013	0.7106	0.7166	0.7212	0.7254
6E ₉ (97 cm ⁻¹)	1.3840	1.4105	1.4283	1.4409	1.4495	1.4574	1.4621
3D(97 cm ⁻¹)	0.7126	0.7207	0.7261	0.7300	0.7326	0.7350	0.7364
Molecular heat	10.1912	10.6110	10.9001	11.1057	11.2536	11.3592	11.4490
Specific heat (cal/gm/deg)	0.1744	0.1815	0.1865	0.1900	0.1925	0.1943	0.1959

results plotted in figure 3 against the experimental results. The greatly improved agreement between theory and experiment which is exhibited in figure 3 makes it clear that the lack of such agreement appearing in figure 2 is due to the frequencies made use of in that case not being the actual frequencies. Indeed, a perfect fit with the experimental data could have been obtained by appropriate alterations in the frequencies made use of in the calculations. But it did not appear worthwhile to attempt to do this for the reason that figures 2 and 3 by themselves make it perfectly clear that the approach to the specific heat theory made in the present investigation is essentially a complete success.

Table 5. Experimental data of specific heats

Temperature	10.9° K	15.3° K	25.1° K	50.7° K	76.4° K	103.1° K
Molecular heat	0.044	0.134	0.658	3.820	6.626	8.424
Specific heat (cal/gm/deg)	0.0008	0.0023	0.0113	0.0654	0.1134	0.1441

Temperature	127.7° K	153.2° K	174.9° K	198.1° K	222.5° K	253.9° K	260.6° K
Molecular heat	9.486	10.162	10.542	10.792	11.006	11.104	11.134
Specific heat (cal/gm/deg)	0.1623	0.1739	0.1804	0.1846	0.1883	0.1900	0.1905

Experimental values of specific heat of NaCl taken from K Clusius, J Goldmann and A Perlick, *Z. Naturforsch.*, **A4**, 424–432 (1949).

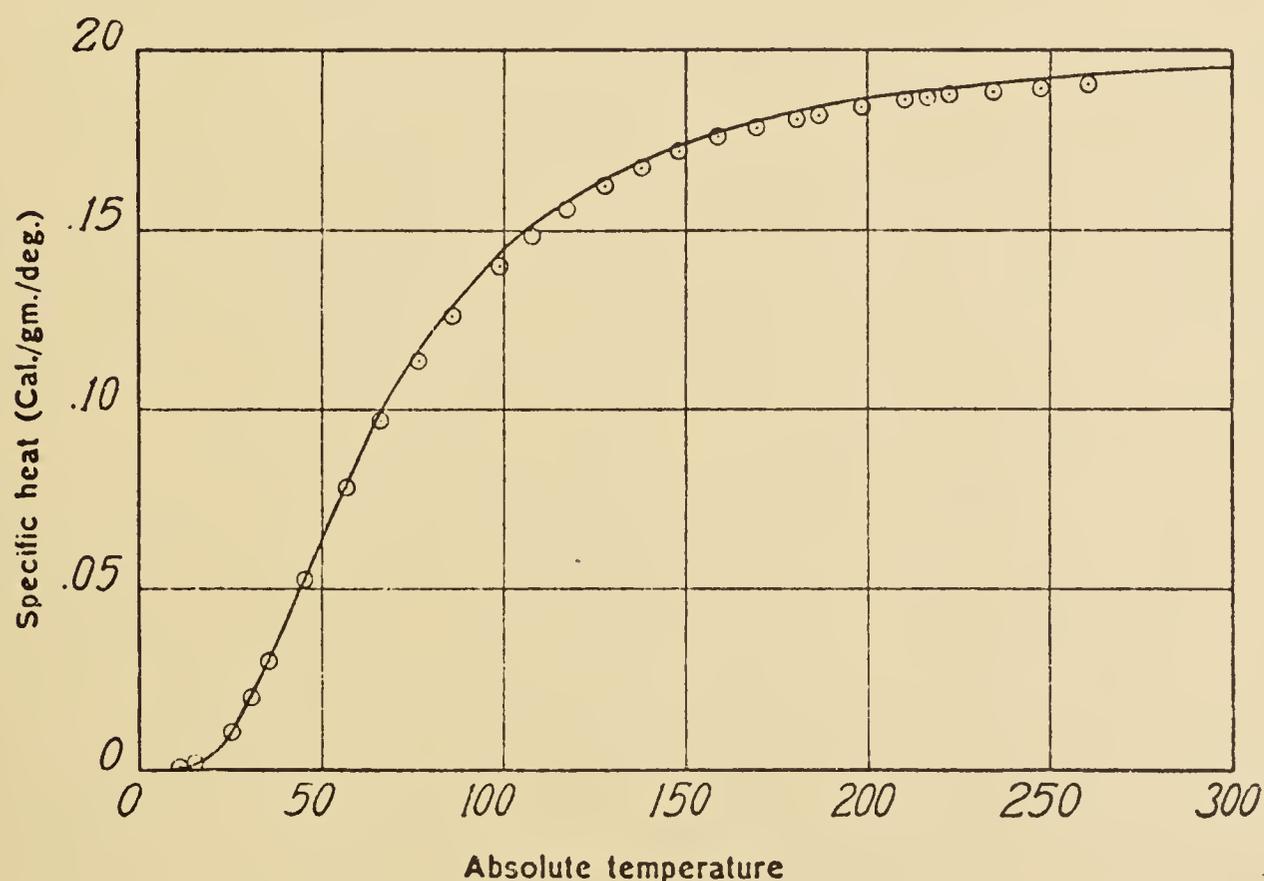


Figure 3. Comparison of theory and experiment. Theory———. Experiment $\odot \odot \odot$.

4. Summary

The spectroscopically determined vibration frequencies of the rock-salt structure are made use of for a theoretical evaluation of its specific heat as a function of

temperature. The results thus obtained are compared with the measured specific heats. The agreement between theory and experiment which emerges demonstrates the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.

The vibration spectrum of lithium fluoride and the evaluation of its specific heat

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1. Introduction

Lithium fluoride crystallises in the cubic system, the crystal structure being similar to that of rock-salt and it also exhibits similar cleavage properties. But in other respects, lithium fluoride differs markedly from rock-salt. Though the atomic weights of both the component elements in lithium fluoride are much smaller, its density is substantially greater than that of rock-salt, being 2.60 as against 2.17. The solubility of lithium fluoride in water is also extremely low. It is clear from these facts that the binding between the metal and halogen atoms is far stronger in lithium fluoride than in rock-salt. Hence the strength of such binding would be quite as important a factor as the lower atomic weights in determining the spectroscopic behaviour of lithium fluoride.

In Memoirs Nos. 127, 128 and 129 of this Institute published in these *Proceedings* in recent months, the author has described studies on the infra-red behaviour of three crystals of simple structure and composition, viz., MgO, NaCl and diamond and shown that the results enable us to determine the characteristic modes and frequencies of free vibration of the atomic nuclei in their structures. It was further shown that on the basis of the spectroscopically determined frequencies and without making use of any other data, it is possible to evaluate the thermal energy of the crystals as a function of the temperature over the entire range extending from the absolute zero upwards up to that at which the specific heat reaches its limiting value. The present memoir aims to accomplish this also in the case of lithium fluoride.

2. The free vibrations of the structure

We may usefully begin by recapitulating briefly the considerations of the same nature as those set out and discussed in much greater detail in the memoirs on MgO and NaCl referred to above. The dispersion, absorption and reflection of

infra-red radiation by a crystal are effects arising from the interaction of the electromagnetic field in the radiation with the structural units forming the crystal. As a first step towards the understanding of these effects, it is necessary to consider the nature of the spectrum of the free or spontaneous vibrations of these structural units. We may deduce their modes and frequencies by the methods of classical mechanics. For this purpose the atomic nuclei may be regarded as simple mass particles and the electronic clouds surrounding them as massless springs which hold the structure together.

It emerges that the vibrational mode of highest frequency of the lithium fluoride structure is one in which the nuclei of lithium and fluorine oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described very simply in terms of the crystal structure. Four of the modes are oscillations of the cubic layers, while the four other modes are the oscillations of the octahedral layers, the movements alternating in phase from layer to layer and being either normal or tangential to those layers. Since the oscillations of the lithium and fluorine nuclei may be either in the same phase or in opposite phases, we have four modes of the cubic layers and four modes of the octahedral layers and hence eight in all. The oscillations of lithium and fluorine nuclei located in the same cubic layers would be coupled with each other and hence would both appear in each of the four modes under reference. But since the lithium and fluorine nuclei appear in distinct layers parallel to the octahedral planes, their oscillations would be independent. In other words, only the layers containing the lithium nuclei would oscillate in two of the modes, the movements being respectively normal and tangential to the layers. Likewise, only the layers containing the fluorine nuclei would oscillate in the two other modes.

3. The vibrational frequencies

The forces which determine the frequencies of vibration in each of the nine modes arise from the displacements relative to an oscillating nucleus of the other nuclei in its neighbourhood. In a first approximation, it is sufficient to consider the interactions between each nucleus and its six immediate neighbours. A special feature of the present case is the great disparity between the atomic weights of lithium and fluorine, which are 6.94 and 19 respectively. Important consequences result from this disparity. The modes in which the lithium nuclei alone oscillate would have notably higher frequencies than those in which the fluorine nuclei alone oscillate. As a further consequence, we should find that the coupled vibrations of the nuclei located in the cubic layers would similarly separate into two pairs, one with higher and the other with lower frequencies of which the values are of the same order of magnitude as those of the modes in which only the lithium and only the fluorine nuclei respectively oscillate. These considerations enable us to arrange the nine modes of free vibration of the structure in a descending order

Table 1. Description of the normal modes

Mode	Description	Degeneracy	Frequency
I	Oscillation of the lithium and fluorine nuclei in opposite phases	3	ν_1
II	Oscillation of the lithium nuclei in the octahedral planes normally	4	ν_2
III	Oscillation of the lithium nuclei in the octahedral planes tangentially	8	ν_3
IV	Oscillation of the lithium and fluorine nuclei in the cubic layers tangentially	6	ν_4
V	Oscillation of the lithium and fluorine nuclei in the cubic layers normally	3	ν_5
VI	Oscillation of the fluorine nuclei in the octahedral planes normally	4	ν_6
VII	Oscillation of the fluorine nuclei in the octahedral planes tangentially	8	ν_7
VIII	Oscillation of the lithium and fluorine nuclei in the cubic layers normally	3	ν_8
IX	Oscillation of the lithium and fluorine nuclei in the cubic layers tangentially	6	ν_9
	Translations	3	$\nu_9 \rightarrow 0$
Total		48	—

of frequency as shown in table 1. On a comparison with the tables of the same kind appearing in the memoirs on MgO and NaCl referred to above, it will be seen that many features are common to all the three cases, a rearrangement appearing only in respect of the modes located near the middle of the table. The principal differences between the three cases are in respect of the relative magnitudes of the various frequencies. In the cases of MgO and NaCl, the frequencies are distributed pretty evenly in their values between the highest and the lowest. In the case of lithium fluoride, on the other hand, four of the frequencies form a group with higher values and the four others form another group with lower values.

In the memoir dealing with the case of magnesium oxide, the dynamical theory which gives explicit formulae for the nine vibration frequencies was developed both in the first and second approximations. Very simple relations between the frequencies ν_1 , ν_2 , ν_3 , ν_6 and ν_7 appear in the first approximation. They are also valid in the second approximation, if we consider only the interactions between each atom of one species and its neighbours of the other species. These relations are, $\nu_1 = k/\mu$, $\nu_2 = \nu_3 = k/m_1$, $\nu_6 = \nu_7 = k/m_2$, where m_1 , m_2 are the masses of the two species of atoms, μ is the reduced mass given by the relation $1/\mu = 1/m_1 + 1/m_2$ and k is the operative force-constant. As will be shown later in this memoir, the infra-red absorption studies with lithium fluoride enable a very

precise determination to be made of the highest vibrational frequency ν_1 . This comes out as 508 cm^{-1} in wave-numbers. From this and the foregoing relations, we obtain $\nu_2 = \nu_3 = 435 \text{ cm}^{-1}$ and $\nu_6 = \nu_7 = 263 \text{ cm}^{-1}$. There are good reasons for assuming that the interaction between each atom and the atoms of the same species surrounding it in the structure of lithium fluoride can be neglected in comparison with the interactions between the atoms of different species. This assumption is equivalent to assuming that the difference between ν_2 and ν_3 and the difference between ν_6 and ν_7 are both unimportant. Since ν_1 is precisely determined, the values for ν_2, ν_3, ν_6 and ν_7 thus calculated can be confidently made use in the evaluation of the thermal energy content. These five frequencies between them account for 27 out of the total of 48 degrees of dynamic freedom. The remaining four frequencies ν_4, ν_5, ν_8 and ν_9 which between them carry 18 degrees of freedom are, as we shall presently see, accessible to observation by infra-red absorption studies.

4. The origin of infra-red activity

As has been stated earlier, the spectrum of free vibrations of the crystal exhibits the frequencies of oscillation of its atomic nuclei about their positions of equilibrium. In determining these frequencies, the massive positively charged atomic nuclei play the major role, while the negatively charged electrons play the subordinate role of holding the nuclei in their positions of equilibrium and of setting up the forces which return the nuclei to those positions when disturbed therefrom.

The spectrum of infra-red absorption and the spectrum of free vibrations are fundamentally different in their nature and origin and cannot therefore be identified with each other. This becomes clear when it is remarked that infra-red absorption represents a transfer of energy from the field of the radiation to the substance of the crystal. For such a transfer to be possible, the field should give rise to a periodic displacement of the mobile electrons present in the structural units of the crystal. This displacement would, on the one hand, excite the vibrations of the structural units and would on the other hand react on the field of radiation and cause its extinction. In these processes, the electrons clearly play the leading role and the atomic nuclei only a subordinate one, thus reversing the position which obtains in the case of the free vibrations.

It is evident that if we assume each nucleus in the structure to carry with it in its movements the full quota of electrons required to neutralise its positive charge, the crystal could display no infra-red activity. It follows that the negative charges of which the movements are the effective cause of infra-red absorption are the electrons which hold the different nuclei together and hence do not participate fully in the movements of any particular nucleus. The movements of these electrons would evidently be determined by the symmetry of their situation and

the symmetry of the movements of the nuclei between which they are located. Lack of such symmetry is clearly indicated as a necessary condition for their being set in motion by the field of the incident radiation and for the excitation of the nuclear vibrations resulting in the transfer of energy from the field to the crystal.

5. Activity of the normal modes

Since the crystal structure of lithium fluoride resembles those of magnesium oxide and of rock-salt, the considerations already set out fully in the two earlier memoirs regarding the infra-red activity of the different normal modes would be applicable also in the case of lithium fluoride. As has already been remarked, however, the case of lithium fluoride presents exceptional features, in particular a great disparity in the atomic weights of the two species of nuclei present in its structure. This disparity carries with it a corresponding disparity in the charges carried by the nuclei. Noteworthy differences in infra-red behaviour stemming from these factors are therefore to be expected. We may usefully here make a comparison between the cases of LiF, MgO and NaCl.

The reduced mass of the nuclei appearing in the formulae for the frequencies of vibration are respectively in these three cases, 5.08, 9.65 and 13.97. Lithium fluoride resembles magnesium oxide in its low solubility in water. Their crystal spacings are not also very different, being 4.01 and 4.203 Å respectively. In these circumstances and since magnesium is divalent whereas lithium is monovalent, the bonding forces in MgO may be presumed to be about twice as strong as in LiF. It follows that the highest vibration frequency would be roughly about the same for lithium fluoride as for magnesium oxide. This indeed, as we shall see, is actually the case. On the other hand, in the case of NaCl, the corresponding frequency is far too low to be accounted for as due solely to the increased mass. The much weaker binding indicated by its solubility in water and the larger crystal spacing has also to be considered.

While the infra-red behaviour of MgO and LiF may thus be similar in some respects, noteworthy differences are also to be expected in view of the factors already alluded to, viz., the great disparity in the masses and charges of the two species of nuclei in the case of lithium fluoride. The disparity in masses would lead to marked differences in the distribution of frequencies in the spectrum. The disparity in the nuclear charges may likewise be expected to result in marked differences in the activities of the different modes, both absolutely and relatively to each other. We may therefore proceed to recall here briefly the behaviour of the different modes in their qualitative aspects as deduced in the earlier memoirs.

The mode of highest frequency in which the lithium and fluorine nuclei oscillate with respect to each other would necessarily be infra-red active, both in the first-order and in the higher orders. In other words, besides the absorption of radiations having nearly the same frequency, we should also expect absorptions

to appear in the regions where the frequency is nearly twice or thrice or four times the frequency of that mode, the strength of such absorption diminishing rapidly with increasing order. Taking the highest frequency in wave-numbers as 508 cm^{-1} and the corresponding wavelength as $19.68\ \mu$, we should expect the absorption of the second-order to appear at $9.84\ \mu$, the absorption of the third-order at about $6.6\ \mu$, and the fourth-order at $4.9\ \mu$. We shall see later that these indications of the theory find support in the observed behaviour of lithium fluoride.

The octahedral modes of vibration listed as II, III, VI and VII in table 1 would be infra-red inactive both in the first and in the higher approximations by reason of the symmetry which they possess, as has already been explained fully in the earlier memoirs. On the other hand, the cubic modes of vibration listed as IV, V, VIII and IX in table 1, though inactive in the first approximation, would be active in the higher approximations. In particular, they may be expected to manifest themselves strongly with doubled frequencies in the infra-red absorption spectrum.

6. Methods of investigation

Following the same procedure as that adopted for magnesium oxide, the infra-red transmission curves of lithium fluoride were recorded using a Leitz spectrophotometer provided with NaCl optics for the spectral range between $1\ \mu$ and $15\ \mu$ and KBr optics for the range between $13\ \mu$ and $24\ \mu$. A clear transparent block of lithium fluoride of $1.8\text{ cm} \times 1.8\text{ cm}$ cross-section was available. From this, a whole series of plates could be obtained by cleavage of different thicknesses. But the optical performance of plates obtained by simple cleavage was not always satisfactory. Hence, it was found to be a better procedure first to obtain a plate of nearly the desired thickness by cleavage and then by grinding and polishing to give its faces a satisfactory finish. In this fashion, it was found possible to carry the investigation down to thicknesses as small as a tenth of a millimetre. The fragility of the material prevents obtaining still thinner plates of adequate size.

The absorption and reflection are both so large at wavelengths greater than $15\ \mu$ that the technique described above then ceases to be inapplicable. Two other procedures analogous to those employed in the case of MgO were accordingly followed. One was to stir very finely ground lithium fluoride into liquid paraffin and to study the transmission by a thin film of the mixture held between KBr plates, balancing it against a similar film of paraffin alone. The second method was to mix a very small quantity of finely divided lithium fluoride with KBr powder and press the mixture in vacuum under high pressure into a flat tablet, the transmission by which was investigated.

Some sixty records in all were made with thirty different absorption paths at fairly close intervals, so as to reveal clearly how the strength of the absorption

varied with the wavelength over the entire spectral range under consideration. The majority of the records were obtained with absorption paths less than one millimetre, for it is in this range, as in the case of magnesium oxide, that the most interesting changes appear in the character of the transmission curves. Nine records out of the large number made are reproduced with this memoir, the selection being made with a view to illustrate the most significant features revealed by the studies.

7. The experimental results

We shall set out the results of the studies by dividing the spectral range covered by them into five different sectors and describing the behaviour of the transmission in these sectors as recorded with different absorbing thicknesses.

I. $4\ \mu$ to $5\ \mu$.—With the maximum thickness employed in these studies, viz., 1.8 cm, the transparency is complete in the wavelength between $1\ \mu$ and $4\ \mu$. But between $4\ \mu$ and $5\ \mu$, the transmission falls by about 5%. But this effect ceases to be observable when the thickness of the plate is five millimetres or less, the curve then running quite horizontally between these wavelengths. It is evident that the absorption between $4\ \mu$ and $5\ \mu$ is extremely weak.

II. $5\ \mu$ to $8\ \mu$.—With an absorption path of 1.8 cm the transmission which is 92% at $5\ \mu$ falls steeply at greater wavelengths, reaching a value of only 18% at $6.5\ \mu$. Beyond this wavelength, the decrease becomes less rapid. The transmission

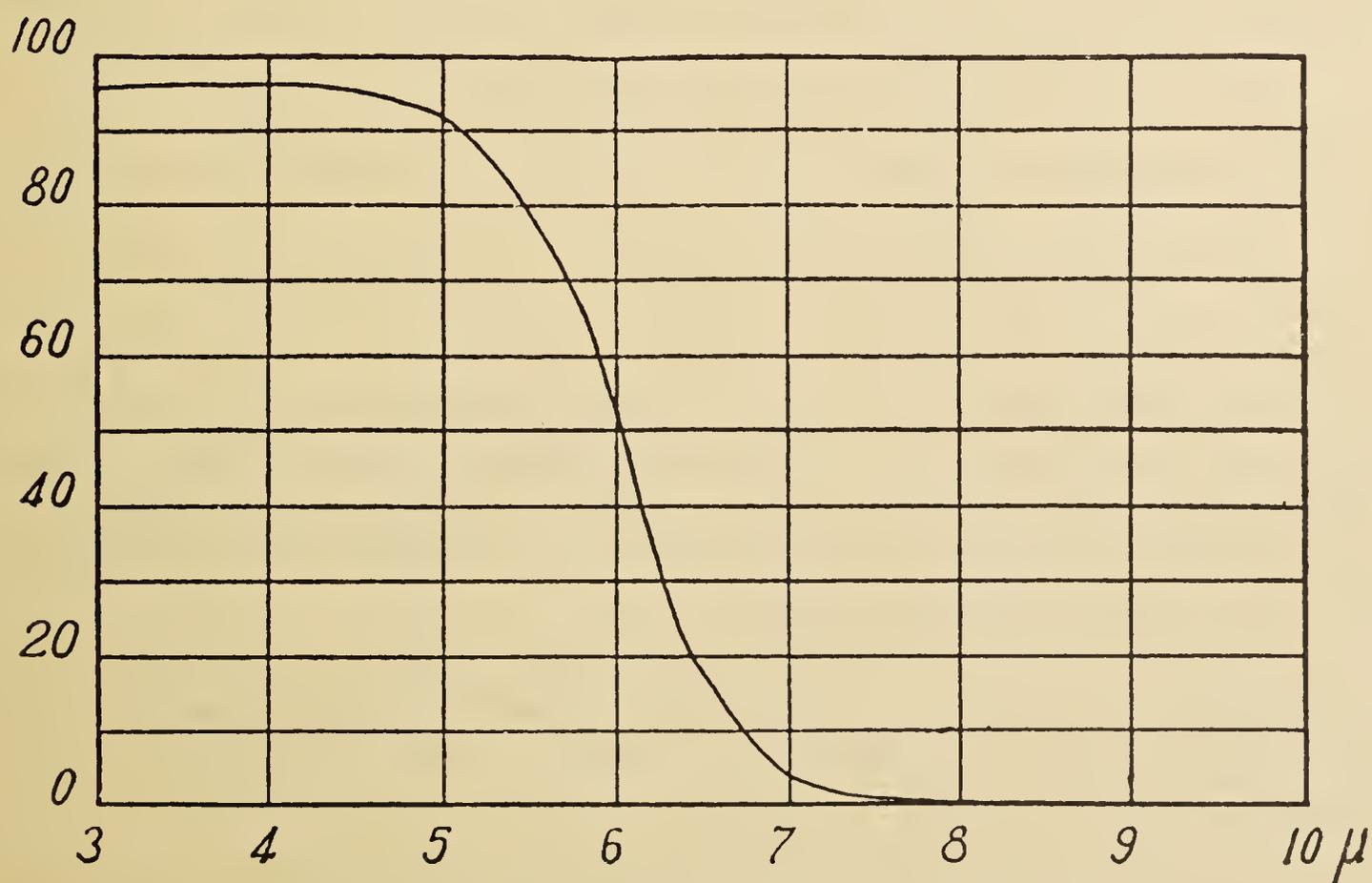


Figure 1. Transmission percentages of block 1.8 centimetres thick.

goes down to 4% at 7μ and is practically zero at 7.5μ . At 8μ and all greater wavelengths there is a complete cut-off. These features are evident in the record reproduced as figure 1 in the text.

When the thickness of the plate traversed by the radiation is reduced from a centimetre or more to a few millimetres, the wavelength at which a cut-off appears moves to 10μ , a sensible transmission then appearing in the region between 8μ and 10μ . These features are noticeable when the absorption path is five millimetres and become increasingly more conspicuous as the thickness is further reduced.

The record of the percentage transmission by a plate 2.92 millimetres thick is reproduced as figure 2 in the text and illustrates the remarks made above. The

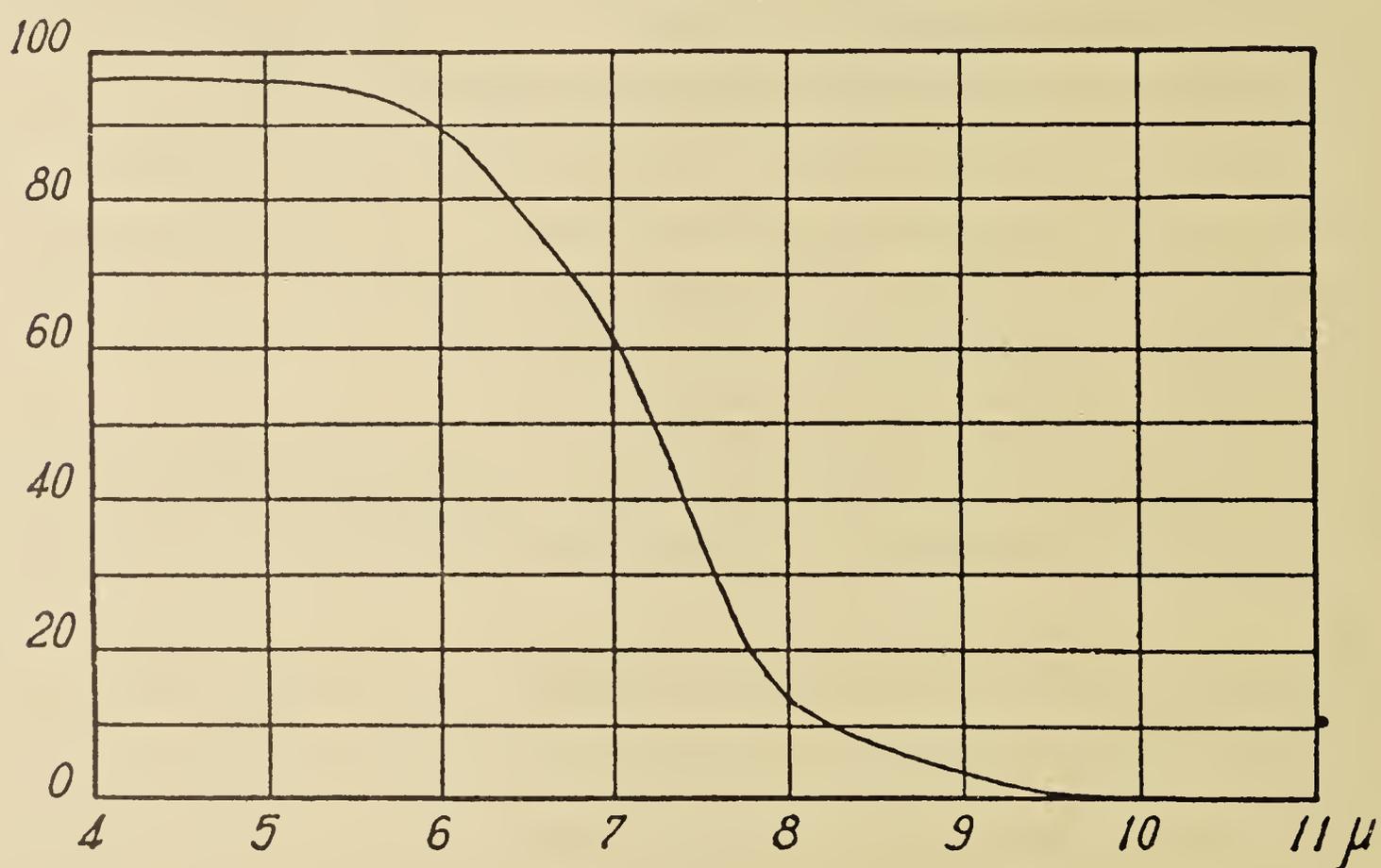


Figure 2. Percentage transmission by plate 2.92 millimetres thick.

curve may be described as consisting of five distinct sectors, viz., a part between 4μ and 5μ where it runs horizontally, a part between 5μ and 6μ where is a gentle fall, then a rapid fall between 6μ and 7μ , a fourth part between 7μ and 8μ where the fall is even more rapid with an inflexion at 7.6μ and finally a gentle slope between 8μ and the cut-off at 10μ .

A comparison of figure 1 with figure 2 shows that the transmission at all wavelengths has notably increased in the latter. The transmission at 6μ has improved from 52% to 90%. The transmission at 7μ has increased from 4% to 62% and that at 8μ from 0% to 13%.

III. 8μ to 10μ .—The record of the transmission appearing in this sector when the cut-off has shifted from 8μ to 10μ initially exhibits a concavity upwards. As

the thickness diminishes, the transmission at $8\ \mu$ improves rapidly. It is zero for an absorption path of 1.8 centimetres, 12% for a thickness of 2.8 millimetres and 50% for a thickness of one millimetre. The slope of the graph between $8\ \mu$ and $10\ \mu$ increases rapidly in consequence and its shape alters at the same time. Its curvature diminishes and the graph appears as a nearly straight line with fairly sharp bends near its two extremities. With smaller thicknesses, the graph is curved in the opposite sense with its convexity directed outwards. But at this stage the cut-off at $10\ \mu$ has disappeared and an appreciable transmission appears beyond that wavelength.

A remarkable series of changes in the form of the transmission curve between $8\ \mu$ and $10\ \mu$ is recorded when the thickness of the plate is progressively reduced from one millimetre down to a tenth of a millimetre. They are depicted in figures 3, 4, 5, 6, 7 and 8. The graph between $8\ \mu$ and $10\ \mu$ does not run continuously into that of the next sector between $10\ \mu$ and $15\ \mu$. Intervening between them appears an arrest or horizontal strip located between $9.8\ \mu$ and $10\ \mu$. As the thickness is progressively reduced, this feature retains its position on the scale of wavelengths but moves upwards. When the thickness is reduced below 0.4 millimetres, it changes its character and develops into a V-shaped depression. This becomes increasingly more conspicuous as the thickness is reduced, and the tip of the depression then appears as a sharp point.

IV. $10\ \mu$ to $15\ \mu$.—The changes appearing in this sector as the absorption thickness is diminished are depicted in figures 3, 4, 5, 6, 7 and 8. When the thickness

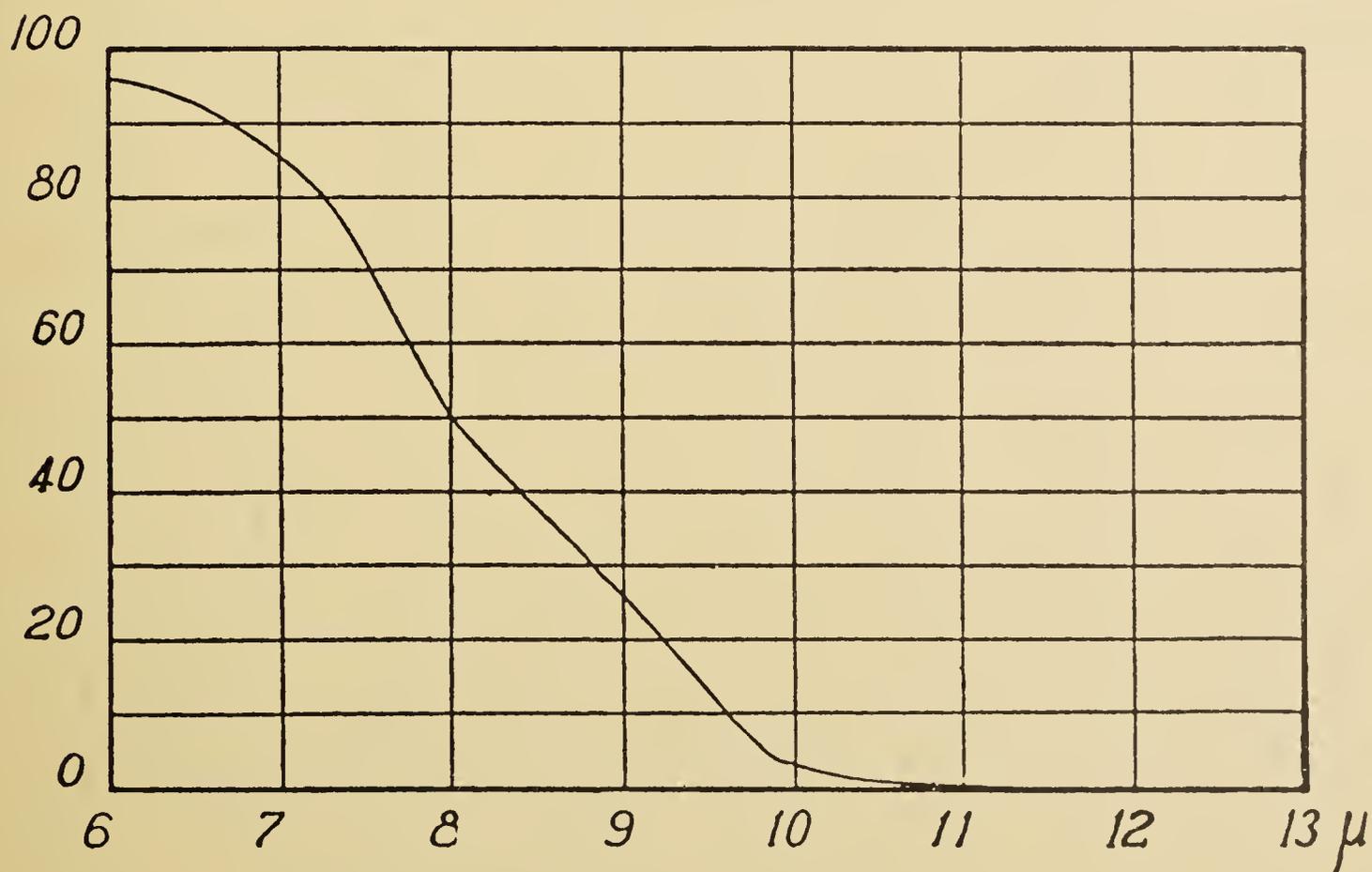


Figure 3. Percentage transmission by plate 1 millimetre thick.

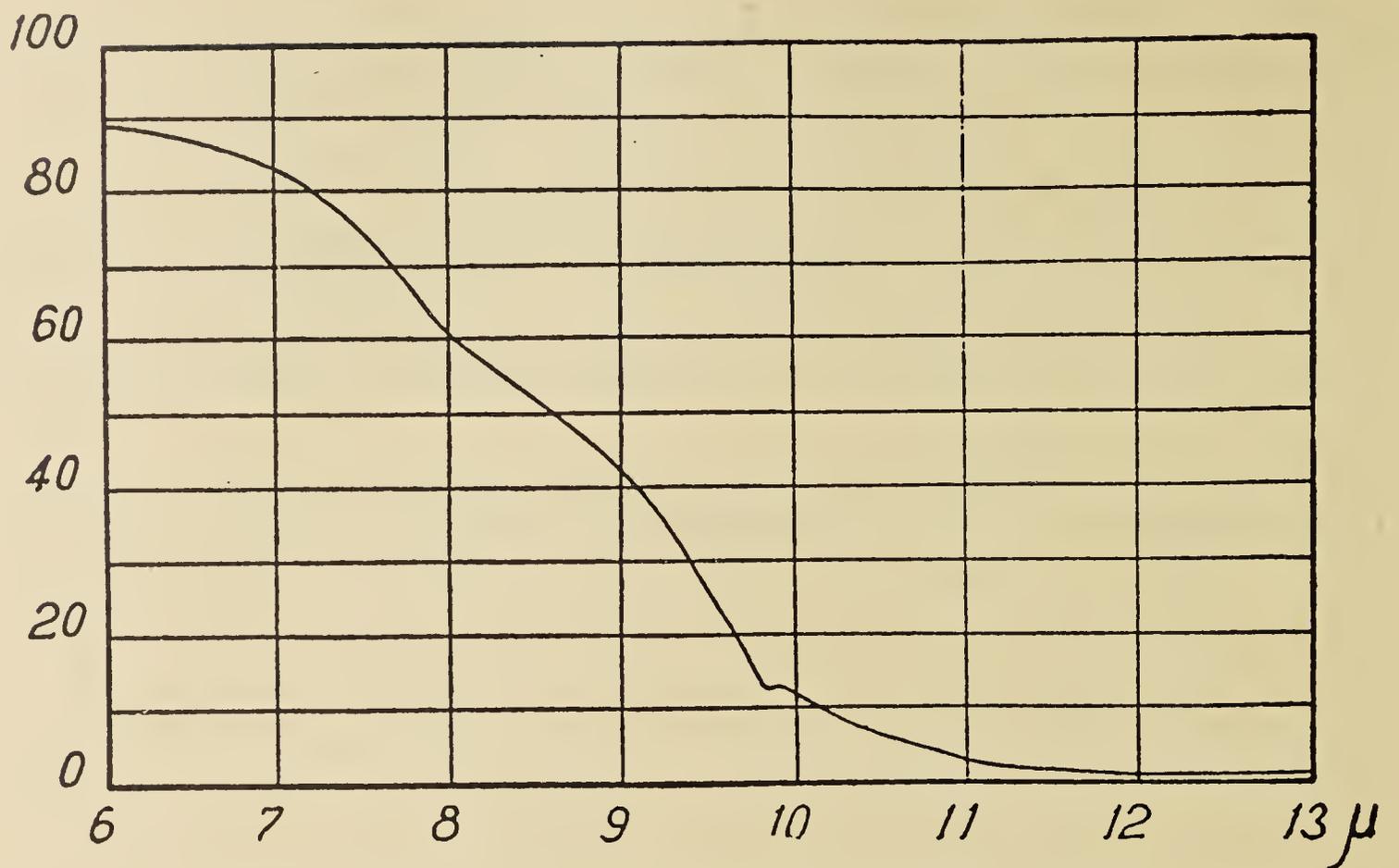


Figure 4. Percentage transmission by plate 0.6 millimetre thick.

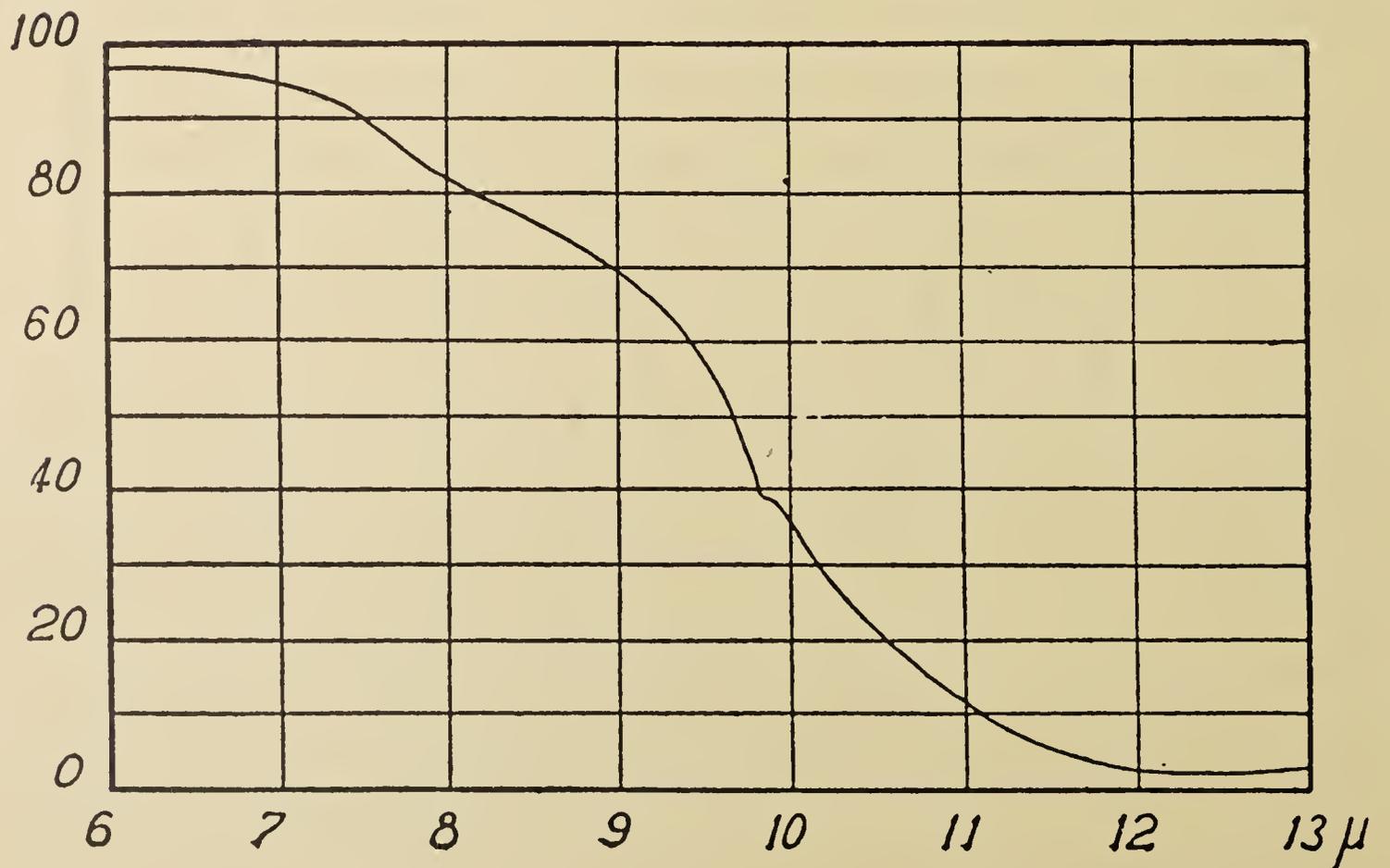


Figure 5. Percentage transmission by plate 0.4 millimetre thick.

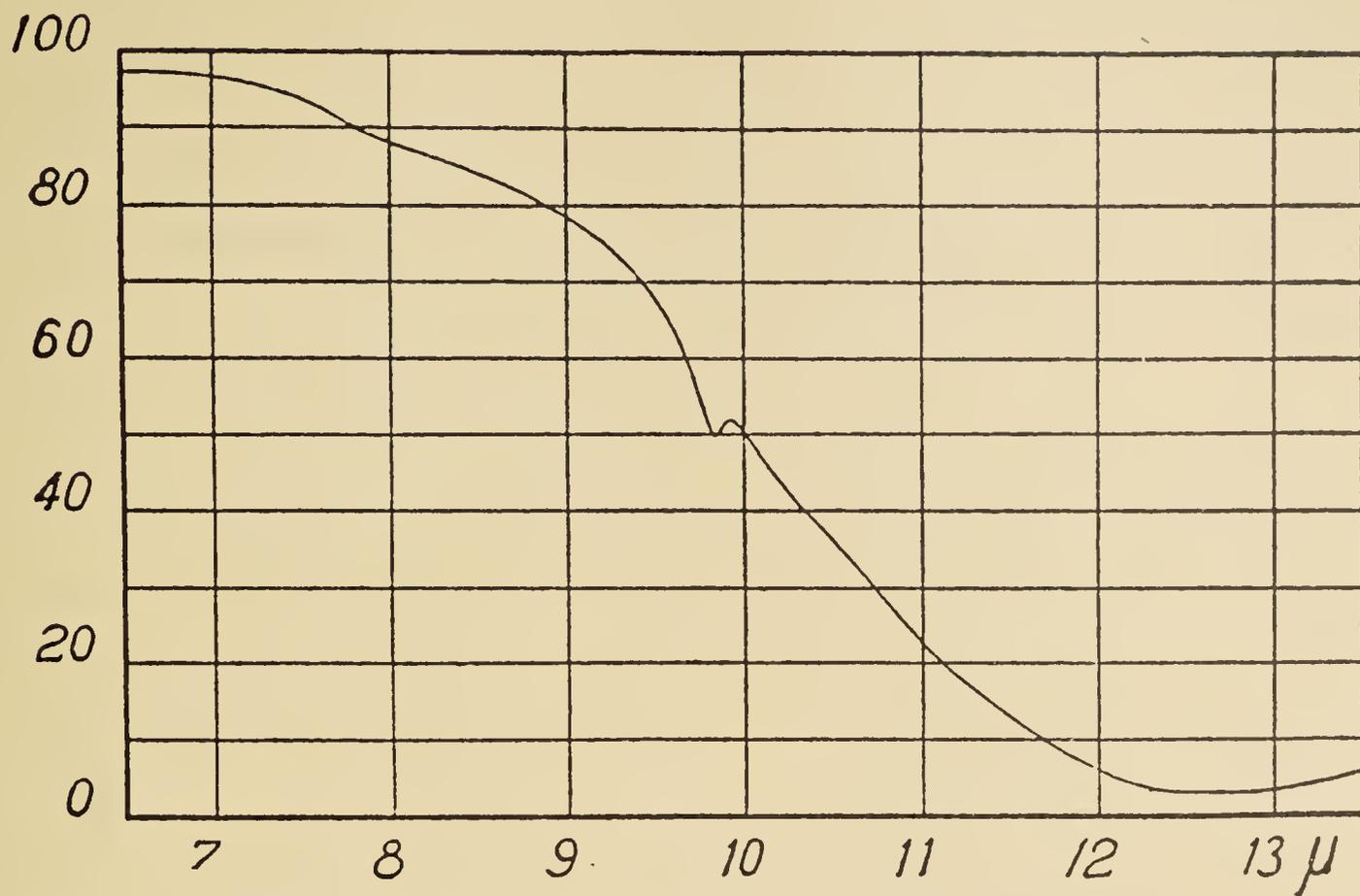


Figure 6. Percentage transmission by plate 0.34 millimetre thick.

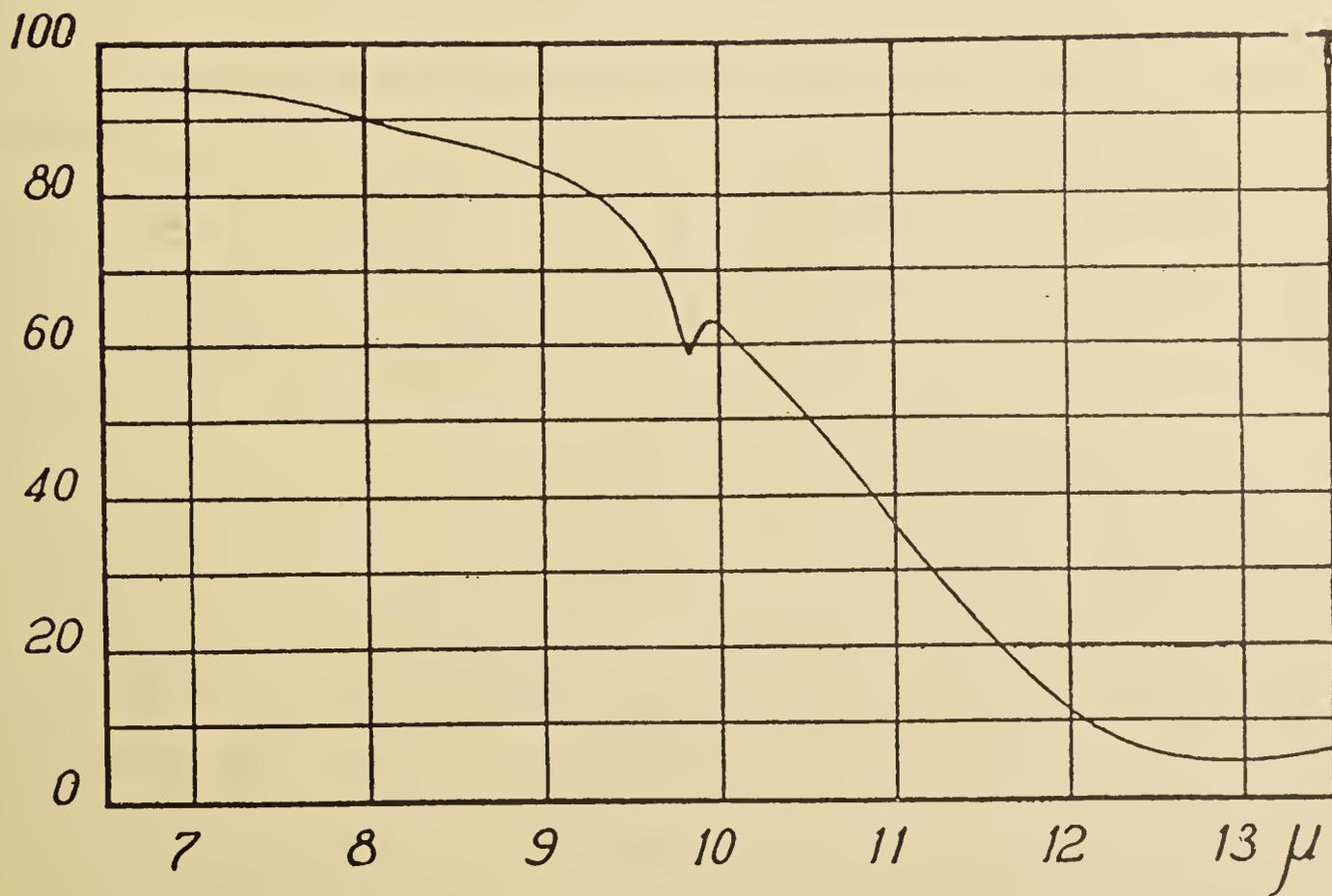


Figure 7. Percentage transmission by plate 0.18 millimetre thick.

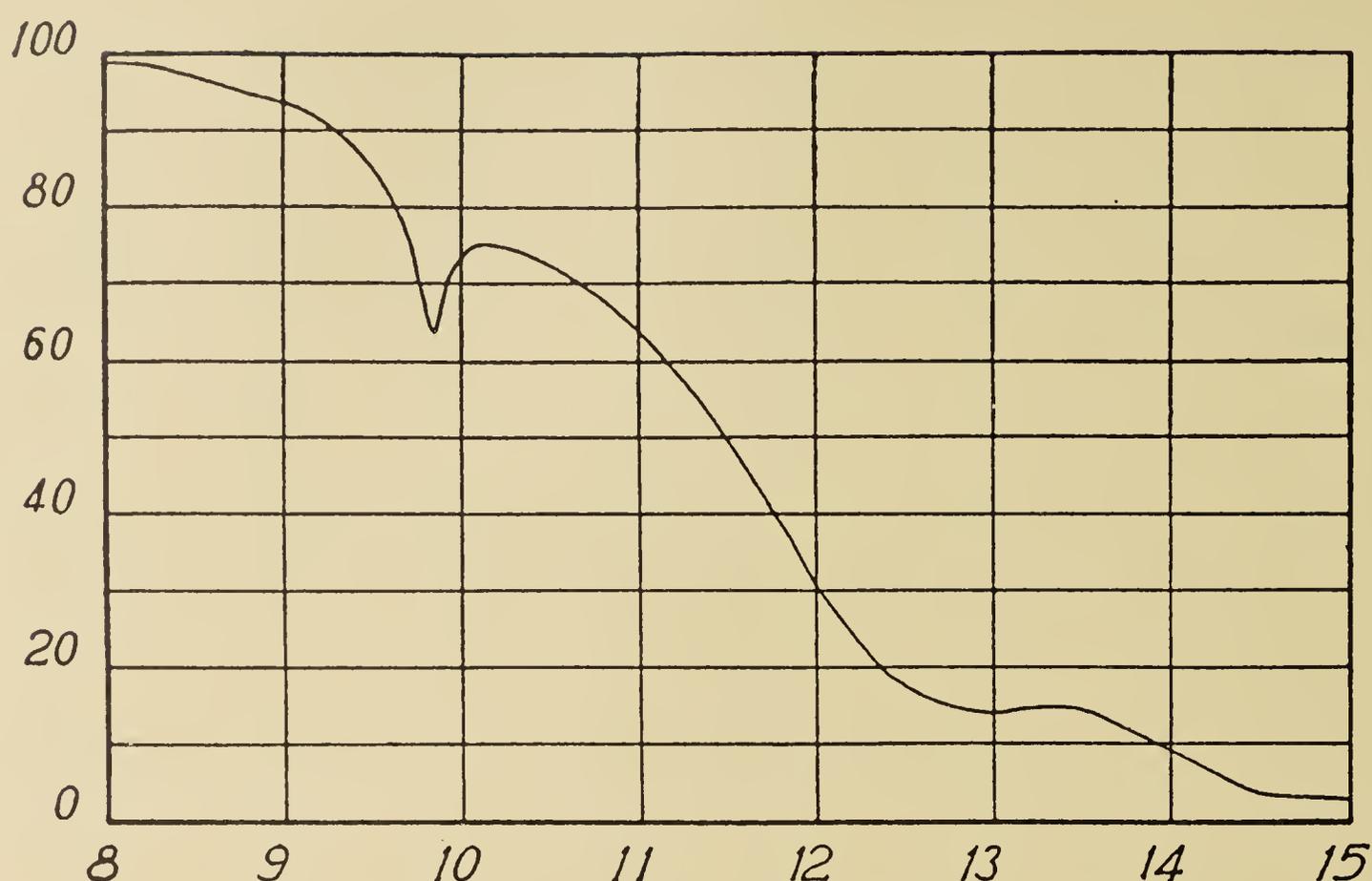


Figure 8. Percentage transmission by plate 0.10 millimetre thick.

is reduced from 2.92 millimetres to 1 millimetre, the cut-off at 10μ moves to 11μ and when it is further reduced the cut-off disappears and a weak transmission is noticed extending up to 13μ and even beyond 13μ . With a thickness of 0.4 millimetre, the wavelength at which the percentage transmission is least may be placed at 12μ . As the thickness is further reduced and the transmission improves, the wavelength at which the transmission is a minimum moves towards longer wavelengths and finally reaches 13μ with the thinnest plates. Beyond 13μ , the transmission is distinctly larger and shows a distinct maximum at about 13.4μ . It then falls off to a much smaller value at 15μ which is the end of the range of the spectrograph with NaCl optics. Records obtained with KBr optics using the thinnest obtainable plates show a transmission of 14% at 13μ , rising to 15% at 13.5μ , and then falling to 12% at 14μ and going down smoothly to zero at 15μ . Beyond 15μ there is a complete cut-off.

V. 15μ to 24μ .—In this range which is accessible to study using KBr optics in the spectrograph, six records were obtained exhibiting the transmission by very small absorption paths in lithium fluoride. Three of these records were made by the pellet technique, three different quantities of finely powdered lithium fluoride, 1 milligram, 0.5 milligram and 0.25 milligram respectively being incorporated with one gram of KBr and pressed into a flat circular tablet the transmission by which was investigated. Three records were also made of the transmission by a layer of liquid paraffin and very finely divided lithium fluoride made up into a paste. One of the records was made with a spacer separating the plates between

which the paste was held. The other two records were made without a spacer but with different quantities of the lithium fluoride in the paste.

The record made by the paste technique with a spacer $30\ \mu$ thick resembled those obtained with the thinnest plates but with the cut-off appearing at $18\ \mu$ instead of at $15\ \mu$. When there was no spacer and the effective thickness of the film was therefore extremely small, a transmission appeared over the entire spectral range. But it was much greater between $13\ \mu$ and $16\ \mu$ than between $18\ \mu$ and $24\ \mu$, a transition appearing between $16\ \mu$ and $18\ \mu$.

The results obtained with the pellet technique are qualitatively similar but quantitatively different with the three different quantities of the lithium fluoride. A large transmission appears between $13\ \mu$ and $16\ \mu$ and a notably smaller transmission between $18\ \mu$ and $24\ \mu$, with a region of transition between $16\ \mu$ and $18\ \mu$. The record made with the half-milligram of lithium fluoride in the pellet is reproduced as figure 9. It exhibits five different features, (a) a region of nearly complete transparency between $13\ \mu$ and $15.5\ \mu$, (b) a region of diminishing transparency between $15.5\ \mu$ and $18\ \mu$, (c) a region of constant transparency between $18\ \mu$ and $20\ \mu$, (d) a region of diminishing transparency between $20\ \mu$ and $22\ \mu$, and finally, a region of nearly constant transparency between $22\ \mu$ and $24\ \mu$.

8. Significance of the results

The most important result which emerges from the present studies is that a sharply-defined minimum of transmission appears at $9.84\ \mu$. This is most strikingly exhibited in figure 8. Its origin is evident from the circumstances in which it is observed. It can indisputably be identified as the second-order absorption due to the mode of vibration listed as having the highest frequency ν_1 in table 1, in other words, the oscillation of the lithium and fluorine nuclei in opposite phases. The wavelength $9.84\ \mu$ corresponds to double this frequency or $2\nu_1$. The sharpness with which it is recorded is an objective demonstration that this free vibration possesses a definite monochromatic frequency.

The frequency ν_1 corresponds to a wavelength $19.68\ \mu$ which is double $9.84\ \mu$. Since the vibrational mode of that frequency is active not only in the first-order but also in the higher orders, we should expect to find evidence of such activity in the appropriate regions of the spectrum, viz., around $6.6\ \mu$ in the third-order, around $4.9\ \mu$ in the fourth-order and around $3.9\ \mu$ in the fifth-order respectively the strength of such activity falling off rapidly with increasing order. This agrees with the recorded results of experiment. The absorption of the fifth-order to be expected at $3.9\ \mu$ is too weak to be recorded with a thickness of $1.8\ \text{cm}$. But there is an observable absorption at $4.9\ \mu$ with that thickness. This, however, disappears when the thickness is reduced to $5\ \text{millimetres}$. On the other hand, the records for various thicknesses exceeding one millimetre all exhibit the third-order absorption at $6.6\ \mu$. The strength of this absorption becomes progressively less

conspicuous as is indicated by the steepness of the fall of the transmission percentage at that wavelength. It finally ceases to be noticeable when the thickness is one millimetre or less. But at these same thicknesses the second-order absorption at 9.84μ is conspicuous and continues to be observable even with the thinnest obtainable plates. It is thereby made evident that the second-order absorption is far more powerful than the third-order effect.

Referring to table 1, we find in it listed as modes IV and V with the frequencies ν_4 and ν_5 the coupled vibrations of the lithium and fluorine appearing in the cubic layers. These two modes are inactive in the first-order but active in all higher orders. From a study of the transmission curves reproduced in the present memoir, we are enabled to recognise the activity of these two modes and locate their characteristic wavelengths at 24μ and 26μ respectively. We should accordingly expect them to give rise to readily observable third-order absorptions as 8μ and 8.7μ respectively and to powerful second-order absorptions at 12μ and 13μ . These absorptions are easily recognisable in the series of figures reproduced above in the text. Indeed, it is clear that these two vibrational modes contribute in a very large measure to the features noticeable in the spectroscopic records of transmission percentage.

We have now to ascertain the frequencies ν_8 and ν_9 of the two other modes of coupled vibration of the lithium and fluorine nuclei appearing in the cubic layers and listed as VIII and IX in table 1. If we take $\nu_8 \approx \nu_9 = 210 \text{ cm}^{-1}$ in wavenumbers, the corresponding wavelength would be 47.6μ . The second-order absorption due to this would appear at 23.8μ . That this is the wavelength at which the minimum transmission appears in figure 9 may be regarded as a justification for the assumed values of ν_8 and ν_9 . Thus, finally, we have in table 2 a list of the nine modes of free vibration of the lithium fluoride structure, their degeneracies, their frequencies and their characteristic wavelengths.

Table 2. Modes and frequencies

Mode	Degeneracy	Frequency cm^{-1}	Wavelength μ
I	3	$\nu_1 = 508$	19.68
II	4	$\nu_2 \approx 435$	23
III	8	$\nu_3 \approx 435$	23
IV	6	$\nu_4 = 417$	24
V	3	$\nu_5 = 384$	26
VI	4	$\nu_6 \approx 263$	38
VII	8	$\nu_7 \approx 263$	38
VIII	3	$\nu_8 \approx 210$	48
IX	6	$\nu_9 \approx 210$	48
Translations	3	$210 \rightarrow 0$	$48 \rightarrow \infty$
Total	48	—	—

9. The rest-strahlen reflections

According to Czerny and Roder (*Ergebn-exakt. Naturwiss.*, 17, 70 (1938)), the reflecting power of a lithium fluoride surface is quite small at $12\ \mu$ and only 20% at $14\ \mu$. It rises steeply to 62% at $15\ \mu$ and thereafter goes up less abruptly to a maximum of 75% at $18\ \mu$. Beyond this again, it dips a little to 72% at $20\ \mu$ and rises to a second maximum of 92% at $26\ \mu$. It then falls off progressively. It is 86% at $30\ \mu$, 68% at $35\ \mu$, 35% at $40\ \mu$ and 28% at $50\ \mu$.

These facts of observation become intelligible when considered in relation to the spectroscopic behaviour of lithium fluoride as elucidated in the present memoir. It is evident from the investigation that the second-order absorptions due to the coupled vibrations in the cubic layers are very powerful. Indeed, from figure 9 it is evident that the second-order activity of modes VIII and IX is actually greater than the first-order activity of mode I. It is therefore to be expected that the reflecting power at $20\ \mu$, though large, would be less than that at greater wavelengths. The appearance of a second and more pronounced maximum at $26\ \mu$ is thus explained.

The slow drop of the reflecting power with increasing wavelength beyond $26\ \mu$ is clearly the result of the co-operation of all the nine modes of free vibration of the structure. Technically, all these modes except the first are infra-red inactive. But this is only in the first approximation. The intense excitation near the surface of the crystal due to the active modes and overtones would necessarily also involve the excitation of all other modes to a greater or less extent determined by the differences between their frequencies and those of the active modes. It follows that

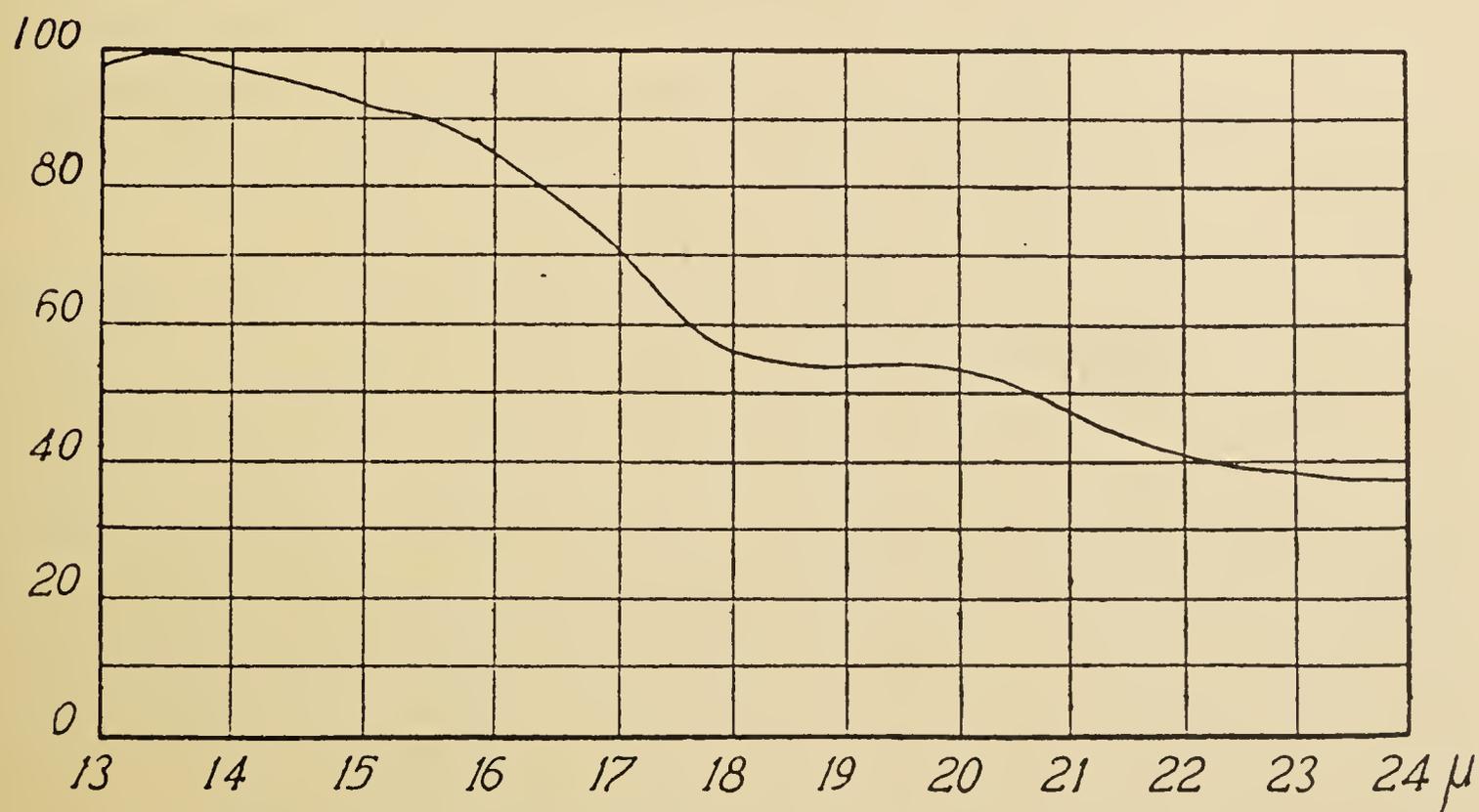


Figure 9. Record of transmission obtained with the pellet technique.

enhanced reflecting power should extend, though with progressively diminishing strength, over the entire range of wavelengths listed in table 2.

10. Computation of the atomic heats

The details of the procedure adopted for the evaluation of the thermal energy of the crystal have already been set out fully in the earlier memoirs dealing with the cases of MgO, NaCl and diamond. It is therefore unnecessary to traverse the same ground here. The unit oscillators with the total of whose energies of vibration we identify the heat content are the 16-atom groups composed of 8 lithium atoms and 8 fluorine atoms. Of the total of 48 degrees of freedom of each such group, 45 degrees of freedom are identified with the modes of their internal vibration, while the 3 remaining degrees of freedom represent their translational movements. These latter again may be identified with the internal vibrations in volume elements of larger size, the frequencies of which diminish as the linear dimensions of the volume elements increase. The number of such volume elements present in the crystal varies inversely as the cube of their linear dimensions. The contribution of these vibrations to the thermal energy content would therefore fall off rapidly as their frequencies go down. The same can be evaluated on the basis of Einstein's theory, except that instead of a summation over a discrete set of frequencies, it appears as an integration based on the distribution law $3N \cdot 3v^2 dv$ derived on the basis of the foregoing considerations, where N represents the number of 16-atom groups contained in the crystal.

Table 3 sets out the computations made for the lower and most interesting part of the temperature range in which the atomic heat goes up rapidly from zero to fairly high values. Table 4 exhibits the computations in the higher range of temperatures up to 500° K. The theoretical calculations are based upon the assumption that the oscillators are harmonic. They also ignore the changes in the frequencies of vibration which accompany the changes in temperature and are related to the thermal expansion of the crystal.

The experimental data have been shown in table 5 for the lower range of temperature and in table 6 for the higher range. The references to the original literature from which the experimental data have been taken have been entered below the respective tables. The specific heats as actually measured are the values at constant pressure. At low temperatures, they do not differ sensibly from the specific heats at constant volume. But it is the latter which can appropriately be compared with the theoretically determined values. Hence it is necessary to compute the specific heats at constant volume from those at constant pressure as experimentally determined. The corrections involve a knowledge of the thermal expansion co-efficient of the crystal and of its isothermal compressibility at the various temperatures.

The thermal expansion of lithium fluoride has been measured over a wide

Table 3. Computation of the atomic heats of LiF

	20° K	40° K	60° K	80° K	100° K	120° K	140° K	160° K	180° K	200° K	220° K	240° K	260° K
3E ₁ (508)	—	—	0.0003	0.0030	0.0124	0.0295	0.0530	0.0794	0.1061	0.1318	0.1559	0.1775	0.1971
12E ₂ (435)	—	0.0001	0.0042	0.0338	0.1054	0.2121	0.3368	0.4604	0.5773	0.6850	0.7784	0.8589	0.9275
6E ₃ (417)	—	—	0.0030	0.0215	0.0633	0.1218	0.1868	0.2518	0.3104	0.3630	0.4074	0.4482	0.4811
3E ₄ (384)	—	0.0001	0.0028	0.0166	0.0435	0.0775	0.1133	0.1464	0.1760	0.2012	0.2224	0.2414	0.2568
12E ₅ (263)	—	0.0094	0.1025	0.2870	0.4932	0.6755	0.8250	0.9413	1.0342	1.1053	1.1642	1.2085	1.2449
9E ₆ (210)	0.0001	0.0309	0.1782	0.3718	0.5398	0.6672	0.7603	0.8315	0.8828	0.9224	0.9533	0.9759	0.9948
3D(210)	0.0081	0.0574	0.1325	0.1969	0.2430	0.2747	0.2966	0.3124	0.3236	0.3321	0.3387	0.3435	0.3476
Atomic heat	0.0082	0.0979	0.4235	0.9306	1.5006	2.0583	2.5718	3.0232	3.4104	3.7408	4.0203	4.2539	4.4498

Table 4. Computation of the atomic heats of LiF

	280° K	300° K	325° K	350° K	375° K	400° K	425° K	450° K	475° K	500° K
3E ₁ (508)	0.2139	0.2293	0.2457	0.2594	0.2713	0.2821	0.2911	0.2982	0.3052	0.3112
12E ₂ (435)	0.9863	1.0377	1.0953	1.1417	1.1802	1.2116	1.2419	1.2653	1.2852	1.3036
6E ₃ (417)	0.5103	0.5342	0.5610	0.5821	0.6011	0.6165	0.6297	0.6412	0.6506	0.6578
3E ₄ (384)	0.2696	0.2805	0.2927	0.3021	0.3105	0.3171	0.3227	0.3277	0.3316	0.3362
12E ₅ (263)	1.2767	1.3013	1.3264	1.3508	1.3672	1.3798	1.3925	1.4025	1.4105	1.4178
9E ₆ (210)	1.0146	1.0254	1.0380	1.0474	1.0564	1.0633	1.0699	1.0748	1.0795	1.0830
3D(210)	0.3511	0.3536	0.3563	0.3582	0.3600	0.3614	0.3628	0.3638	0.3647	0.3655
Atomic heat	4.6225	4.7620	4.9154	5.0417	5.1467	5.2318	5.3106	5.3735	5.4273	5.4751

Table 5. Comparison of the experimental and theoretical values of the atomic heats (C_v) of LiF

Temperature	20° K	40° K	60° K	80° K	100° K	120° K	140° K	160° K	180° K	200° K	220° K	240° K	260° K
Interpolated experimental values	0.0086	0.1030	0.4110	0.9340	1.5250	2.1270	2.6650	3.1220	3.5080	3.8150	4.0760	4.2840	4.4580
Calculated values	0.0082	0.0979	0.4235	0.9306	1.5006	2.0583	2.5718	3.0232	3.4104	3.7408	4.0203	4.2539	4.4498

Experimental values of the atomic heats of LiF from K Clusins, J Goldmann and A Perliek, *Z. Naturforsch.*, **A4**, 424-432 (1949).

Table 6. Comparison of the experimental and theoretical values of the atomic heats of LiF

Temperature	300° K	325° K	350° K	375° K	400° K	425° K	450° K	475° K	500° K
Experimental values of C_p	5.0210	5.1885	5.3335	5.4595	5.5710	5.6705	5.7600	5.8410	5.9155
Corrected for C_v	4.7724	4.9110	5.0245	5.1165	5.1908	5.2500	5.2951	5.3281	5.3496
Calculated values	4.7620	4.9154	5.0417	5.1467	5.2318	5.3106	5.3735	5.4273	5.4751

Experimental values of the atomic heats of LiF from T B Douglas and J L Dever, *J. Am. Chem. Soc.* **76**, 4826 (1954).

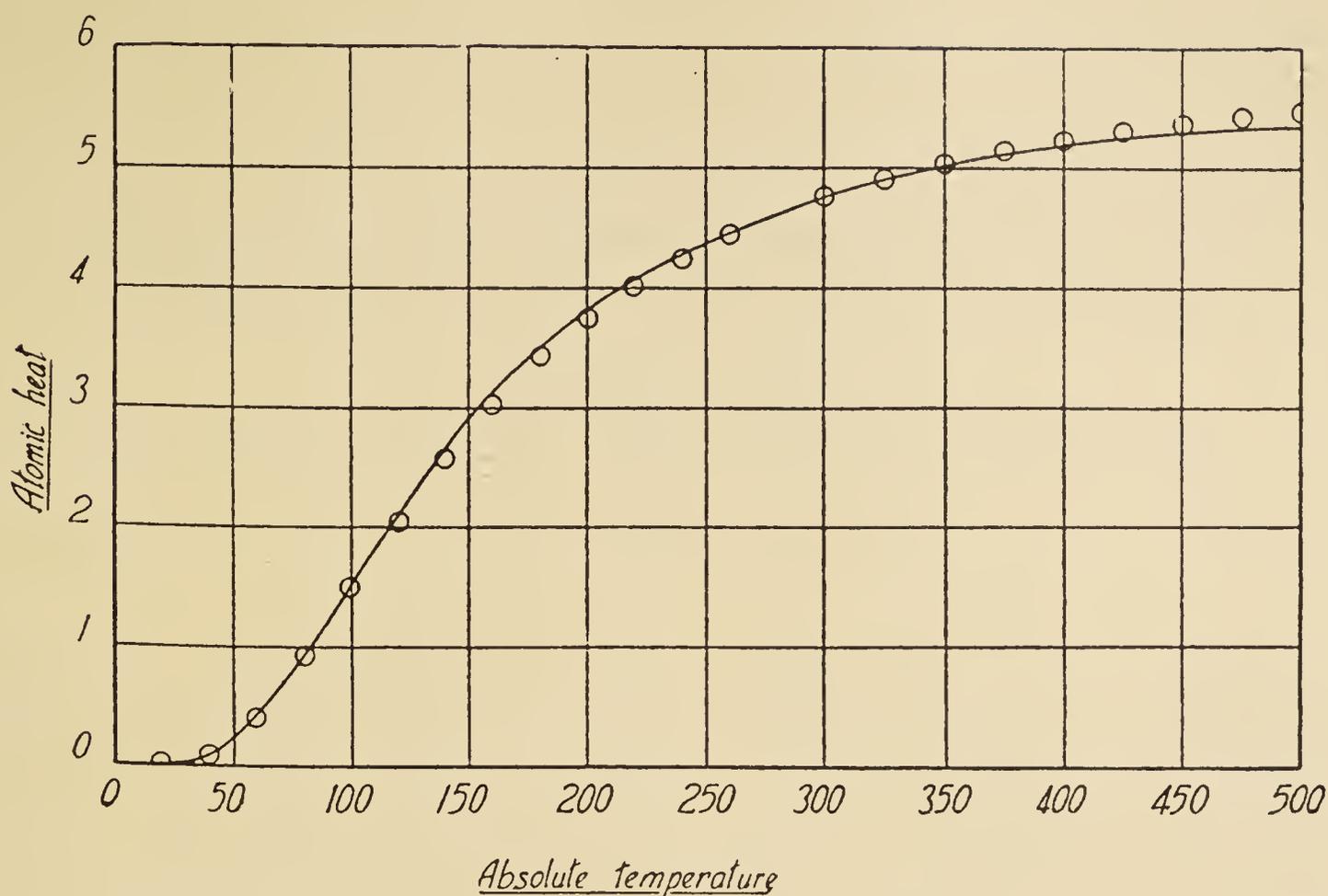


Figure 10. Comparison of the theoretically calculated and experimentally determined atomic heats. Experimental results———; theoretical values ○○○○.

range of temperatures. The compressibility, however, has only been determined near room temperatures. Some uncertainty is thereby introduced in effecting the reduction from C_p to C_v .

Tables 5 and 6 show a satisfactory over-all agreement between the theoretically computed and experimentally determined values of atomic heat over the entire range of temperature from absolute zero up to 500°K . This agreement is graphically exhibited in figure 10.

Summary

The records of the transmission percentages of infra-red radiation by thin plates of lithium fluoride enable the frequency of the vibration of the lithium and fluorine nuclei against each other in opposite phases to be precisely determined. The frequencies of the four inactive modes can be computed therefrom. Four other modes are active as overtones and their frequencies can be directly determined from the records. A theoretical computation of the specific heat of lithium fluoride on the basis of the spectroscopic data alone thus becomes possible. A very satisfactory agreement emerges between the theoretically computed and experimentally determined values of the atomic heats of the crystal over the entire range of temperatures from absolute zero to 500°K .

The specific heats of the alkali halides and their spectroscopic behaviour—Part I. Introduction

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The compounds of the alkali metals with the halogen elements are crystalline solids which are of great interest alike from the theoretical and experimental standpoints. Sixteen of them, viz., the compounds of lithium, sodium, potassium and rubidium respectively with fluorine, chlorine, bromine and iodine possess crystal structures similar to each other, the typical case being rock-salt or NaCl. The elucidation of the thermal properties of the alkali halides in relation to their spectroscopic behaviour is the subject of the present memoir. Since the halides of caesium possess a different structure, they will be left out of consideration in our discussions.

Though all the sixteen halides are cubic crystals having a common structural pattern, they nevertheless exhibit a wide range of physical behaviour. The fluorides, in particular, have distinctive properties. Their melting points are notably higher than those of the corresponding chlorides, bromides and iodides, thereby indicating a stronger binding between the metal and halogen atoms. This is also very clearly shown by a comparison of the elastic behaviours of all the sixteen halides, the determinations of which by the ultrasonic diffraction method have been recently published (reference 1). Table 1 below reproduces the data reported by the authors quoted, except that instead of the compressibility, the table shows the bulk-modulus K which is its reciprocal and is taken equal to $(C_{11} + 2C_{12})/3$.

A study of the figures appearing in table 1 is instructive. It will be seen that the elastic constants diminish rapidly in the sequence of the alkali metals lithium, sodium, potassium and rubidium and even more rapidly in the sequence of the halogens, fluorine, chlorine, bromine and iodine. The fall in passing from the fluorides to the chlorides is particularly striking. It is also noteworthy that the shear-modulus C_{44} is of the same order of magnitude as the bulk modulus K in the case of the lithium halides. But it is much the smaller of the two in the case of the halides of the other alkali metals.

The rock-salt structure is one of exceptional simplicity. The characteristic modes of free vibration of the atoms in it can therefore be readily established and

described completely in terms related to the geometry of the structure. The frequencies of the free vibrations would naturally depend on the masses of both the metal and halogen atoms and also on the strength of the binding between them which, as is indicated by the figures in table 1, would be very different in the different cases. It follows that the spectrum of the characteristic frequencies would vary from halide to halide in a distinctive fashion.

Table 1. Lattice spacings and elastic moduli
(Elastic moduli in 10^{11} erg/cm²; Lattice constant in Å; Temperature 22° C)

Substance	C_{11}	C_{12}	C_{44}	K	Lattice constant
LiF	11.35	4.80	6.35	6.99	4.01
LiCl	4.94	2.26	2.49	3.15	5.14
LiBr	3.94	1.88	1.91	2.56	5.49
LiI	2.85	1.40	1.35	1.89	6.00
NaF	9.71	2.43	2.80	4.85	4.62
NaCl	4.93	1.31	1.275	2.52	5.627
NaBr	4.02	1.15	0.99	2.11	5.94
NaI	3.035	0.90	0.72	1.61	6.46
KF	6.58	1.49	1.28	3.18	5.33
KCl	4.08	0.69	0.635	1.82	6.28
KBr	3.49	0.58	0.51	1.55	6.578
KI	2.775	0.47	0.38	1.24	7.052
RbF	5.7	1.25	0.91	2.73	5.63
RbCl	3.645	0.61	0.475	1.62	6.571
RbBr	3.185	0.48	0.385	1.38	6.868
RbI	2.585	0.375	0.281	1.11	7.325

It will be shown in this memoir that the spectrum of frequencies of atomic vibration can be evaluated for all the sixteen halides by making use of the data shown in table 1 and that on the basis of such evaluation, the specific heats of each halide can be determined in terms of the temperature over the entire range from the absolute zero upwards.

The evaluation of the modes and frequencies of atomic vibration enables us to go further and predict the spectroscopic behaviour of the halides. We are here concerned with two different problems which will be considered separately. The first is the absorption, reflection and dispersion of infra-red radiation incident on the crystal. The second problem concerns the frequency shifts observed when monochromatic light of sufficient intensity traverses the crystal and the scattered radiations are investigated spectroscopically.

As the object of the memoir is to demonstrate the power and success of the theoretical approach which has been adopted, we shall naturally proceed to compare the results to which it leads with the facts of observation in those cases in which the necessary data are available.

Table 2. Some physical constants

Substance	Density	Refractive index (589 m μ)	Refractive index (254 m μ)	Melting point	Solubility (in 100 parts)
LiF	2.6	1.3915	1.4179	870° C	0.27
LiCl	2.07	1.662	—	613° C	45
LiBr	3.46	1.784	—	547° C	143
LiI	4.06	1.955	—	446° C	151
NaF	2.79	1.3258	1.37	992° C	4.2
NaCl	2.17	1.544	1.653	801° C	36
NaBr	3.20	1.6412	1.8323	755° C	80
NaI	3.67	1.7745	—	651° C	159
KF	2.48	1.361	—	880° C	92
KCl	1.98	1.490	1.588	790° C	28
KBr	2.75	1.5596	1.7181	730° C	54
KI	3.13	1.6674	2.0169	723° C	127
RbF	2.88	1.3960	—	760° C	130
RbCl	2.76	1.4936	1.5905	715° C	77
RbBr	3.35	1.5528	—	682° C	98
RbI	3.55	1.6474	—	652° C	138

We may conclude this introductory part of the memoir by tabulating some further physical data of interest for each of the sixteen alkali halides. Table 2 exhibits for each halide the following physical constants: (a) the density, (b) the refractive index in the visible spectrum, (c) the refractive index in ultra-violet, (d) the melting point, and (e) the solubility in water at room temperature.

We may draw attention to some significant features noticeable in table 2. There is a large drop in density when we pass from the fluoride to the chloride in each case. This is in striking contrast with the increases in the density in passing from the chloride to the bromide and then to the iodide. This increase in density is a clear indication of the great strength of the binding between the metal and the halogen atoms in the fluorides. As has already been remarked, the same feature is conspicuous from the data for the elastic moduli listed earlier in table 1.

The refractive index of the fluorides is invariably lower than that of the other halides, and it is noteworthy that this feature appears despite the high density of the fluorides. The dispersive power of the fluorides as indicated by the difference of the refractive indices in the visible and ultra-violet is also small. *Per contra*, it is conspicuously large for the other halides and particularly so in the cases of the bromides and iodides.

The solubility in water of the alkali halides shows large variations in the different cases. Lithium fluoride is only sparingly soluble, in striking contrast with the behaviour of the other halides of lithium. The sodium salts exhibit a regular sequence in their solubilities. But this is not so in the case of the halides of

potassium and rubidium, their fluorides being actually more soluble than the chlorides and bromides.

Summary

The sixteen alkali halides which form the subject of the memoir, viz., the fluorides, chlorides, bromides and iodides of lithium, sodium, potassium and rubidium all possess the rock-salt structure but exhibit a remarkable diversity in their physical properties. Especially notable are the values of their elastic constants, the published determinations of which indicate striking differences in the nature and strength of the binding between the metal and the halogen atoms in the various cases.

Reference

1. Spangenberg K and Haussühl S *Z. Kristallogr.* **109** 422 (1957).

The specific heats of the alkali halides and their spectroscopic behaviour—Part II. The free modes of atomic vibration

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A well known theorem in classical dynamics states that all the possible small vibrations of a conservative dynamical system about a position of stable equilibrium may be represented as a superposition of certain modes of vibration designated as the normal modes of the system. The number of normal modes is equal to the number of degrees of dynamical freedom of the system and in each such mode, the particles of the system execute harmonic vibrations with a common frequency characteristic of the mode and their phases are all the same or opposite, in other words, they all pass simultaneously through their positions of equilibrium. This identity or opposition of phase is a fundamental property of a normal mode of vibration. In the absence of this phase-relationship, the possible movements of the particles would be infinitely varied and hence incapable of enumeration.

The theory of the specific heats of crystals has, of necessity, to be based on the theorem in classical mechanics stated above and on the principles of the quantum theory and of thermodynamics. It identifies the thermal energy of the crystal with the sum-total of the quanta of vibrational energy of the oscillators of various frequencies constituting the crystal. If these oscillators are correctly identified and enumerated, their total number should come out as equal to the number of degrees of dynamical freedom of the system, viz., thrice the number of atoms comprised in the crystal. This remark serves to remind us that the particles with which we are concerned in the specific heat problem are the atoms. It also emphasises that the vibrational modes enumerated should be normal modes, viz., modes in which the individual atoms all vibrate with the same frequency and in the same or opposite phases. It thus becomes clear that the core of the specific heat problem is the answer to the following question: do the atoms located in the structure of the crystal possess any normal modes of vibration having the stated characters and if so, what is the number of such modes and how is their number related to the number of atoms comprised in each unit cell of the crystal structure?

The questions raised above can be answered in the following manner. We make use of the fundamental property of a crystal that the structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Since each atom comes into coincidence with an equivalent atom in the next cell, all physical properties of the crystal determined by the atomic locations and the atomic interactions should also remain unaltered. Since the modes of free vibration of the structure constitute such a property, we are justified in the inference that a vibration having the stated characters of a normal mode should remain unaltered and continue to be a normal mode following a unit translation. This can happen in two ways. Equivalent atoms brought into coincidence can have identical amplitudes and phases of vibration. Alternatively, their amplitudes can be the same but all the phases are reversed. (In the latter case, the original phases are regained after a half-period and hence the normal mode is effectively unaltered.)

The two alternative possibilities indicated above arise in respect of a unit translation along each of the three axes of the lattice. Since these are independent of each other, we have $2 \times 2 \times 2 = 8$ different possibilities in all. In each of these 8 possibilities, the amplitudes of vibration of the atoms in the cells adjoining a particular cell are the same as those of the equivalent atoms in that cell. Hence, if there are n atoms in each unit cell of the structure, their $3n$ equations of motion involving their interactions with the surrounding atoms which are assumed to be proportional to their relative displacements contain only $3n$ displacement co-ordinates. Hence the equations of motion can be completely solved, the solutions obtained giving us the frequencies and the ratios of the atomic displacements along each of the co-ordinate axes.

Considering all the eight possibilities referred to above, we have $8 \times 3n = 24n$ distinct solutions or normal modes of vibration. In $3n$ of these modes, the vibrations of equivalent atoms have the same phase in the adjoining cells, while in the remaining $21n$ modes, they appear with alternating phases along one or two or all three axes of the lattice. By the nature of the case, however, 3 out of the $3n$ modes have a zero frequency, in other words, represent simple translations. Hence we have only $(3n - 3)$ normal modes properly so-called of the first species and $21n$ normal modes of the second species. When $n = 1$, in other words, when the atoms in the crystal occupy the points of a simple Bravais lattice, we have only 21 modes of the second species, besides 3 translations. When $n = 2$, we have besides the 3 translations, 3 normal modes of the first species and 42 normal modes of the second species.

When the crystal exhibits a high degree of symmetry, e.g., cubic symmetry, the number of normal modes remains the same, but many of the modes are similar to each other and the number of *distinct* frequencies is thereby greatly reduced. In the particular case of the alkali halides, the 3 normal modes of the first species exhibit a single triply-degenerate frequency, while the remaining 42 modes have only 8 distinct frequencies, viz., two frequencies each with a degeneracy of 4, two

frequencies each having a degeneracy of 8, two frequencies each with a degeneracy of 3 and two others each with a degeneracy of 6, thus totalling up to 42 distinct modes of the second species.

The degeneracies listed above arise by reason of the geometric similarity of the various sets of normal modes. The triply degenerate frequency of the first species represents an oscillation of the two sets of non-equivalent atoms along one or another of the three cubic axes. The triply degenerate frequencies of the second species represent vibrations of the two sets of non-equivalent atoms lying in the cubic planes normally to themselves. The six-fold degenerate frequencies similarly represent vibrations of the layers of atoms appearing in the cubic planes tangentially to themselves. Four-fold degeneracy arises when the layers of atoms parallel to the octahedral planes move normally to themselves. Eight-fold degeneracy arises when the atoms in the octahedral layers move tangentially to those layers.

The geometry of the various modes of vibration can be readily established. We begin with the case of a simple face-centred cubic lattice, the 24 normal modes of which are listed below, the phases of oscillation alternating in the successive planes.

Description of the modes	Degeneracy
1. Simple translations	3
2. Oscillations normal to the cubic planes	3
3. Oscillations tangential to the cubic planes	6
4. Oscillations normal to the octahedral planes	4
5. Oscillations tangential to the octahedral planes	8
Total	24

The foregoing descriptions can be readily derived by considering the atomic movements in a face-centred cubic lattice for each of the 8 different possibilities regarding their phase-relationships discussed earlier. The directions of atomic movement are those indicated by the symmetry of the crystal.

In the alkali halides, we are concerned with two similar face-centred cubic lattices which interpenetrate each other, their points being occupied respectively by the metal and the halogen atoms. In the cubic planes of the resulting structure, the metal and halogen atoms appear interspersed in the same layers, while in the octahedral planes, they appear in distinct but equidistant layers. Since the phases of oscillation of the metal and halogen atoms may be either the same or the opposite, the 24 modes listed above are doubled up, giving us 48 modes in all. The three translations of each lattice separately are replaced by three translations in which the two lattices move together in the same phase, and by three oscillations

respectively along the three cubic axes in which the two lattices move in opposite phases.

	Degeneracy
I. Oscillation of the metal and halogen atoms in opposite phases	3
II. Coupled oscillations of the metal and halogen atoms in the cubic planes	
(a) Tangential to the planes in opposite phases	6
(b) Normal to the planes in the same phase	3
(c) Normal to the planes in opposite phases	3
(d) Tangential to the planes in the same phase	6
III. Oscillations of the atoms appearing in the octahedral layers	
(a) Lighter atoms normal to the planes	4
(b) Lighter atoms tangential to the planes	8
(c) Heavier atoms normal to the planes	4
(d) Heavier atoms tangential to the planes	8
IV. Translations of both lattices in the same phase	3
	<hr/>
Total	48
	<hr/>

The nine modes have been listed in the foregoing table, the four vibrations of the cubic layers and the four vibrations of the octahedral layers being arranged amongst themselves in the descending order of their frequencies of vibration as indicated by the dynamical theory to be presented later in the memoir.

Summary

It is shown that crystals having the rock-salt structure have nine different frequencies of atomic vibration exhibiting the features of normal modes. One of them is an oscillation of the metal and halogen atoms in opposite phases. Four others are coupled oscillations of the atoms appearing in the cubic layers, while the remaining four are oscillations of the atoms in the octahedral layers. The oscillations in these eight modes alternate in phase from layer to layer and are respectively normal or tangential to those layers.

The specific heats of the alkali halides and their spectroscopic behaviour—Part III. The interatomic forces

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We shall now consider the problem of evaluating the frequency of each of the nine normal modes of vibration of the atoms described in part II of this memoir. These frequencies are determined by the masses of the atoms, the geometric characters of the vibration and especially by the forces of interaction between the atoms brought into play by reason of their displacements. The evaluation of these forces is indeed the essence of the problem.

We may begin by recalling the characteristic features of the crystal structure of the alkali halides. Each metal atom has six halogen atoms as its immediate neighbours. These are situated on either side of it on the three cubic axes and at the same distance in each case. Likewise, each halogen atom has six metal atoms as its immediate neighbours, also located on the three cubic axes in the same manner. This grouping of the metal and halogen atoms around each other with cubic symmetry determines the architecture of the crystal, and the forces which result in such grouping would necessarily play the leading role in determining the physical properties of the solid.

As has been remarked above, the forces which determine the frequencies of atomic vibration arise by reason of their displacements from their positions of equilibrium. Since the atoms are held together in the crystal by their mutual interactions, what we are really concerned with are their *relative* displacements. We are justified in assuming that the forces which determine the frequencies of vibration of the structure would be principally those due to the displacements relative to each other of the metal and halogen atoms held together in the structure in the manner described above. Considering a particular pair of metal and halogen atoms, it is evident from considerations of symmetry that if a metal atom is displaced with respect to the adjacent halogen atom *along* the cubic axis on which they both lie, the restoring force would also be along the same axis and that there would be no transverse components. As a first approximation this restoring force may be taken to be proportional to the relative displacement, and if the distance between the two atoms is denoted by d (which is half the lattice

spacings in the crystal) and the same is increased or diminished by Δ , the restoring force may be written as $\alpha\Delta$, where α is the force-constant involved.

Likewise, considering a relative displacement Δ of the two atoms *transverse* to the cubic axes on which they both lie, considerations of symmetry indicate that the restoring force would be parallel to the displacement and hence transverse to the cubic axis, and that there would be no components along the two other perpendicular cubic axes. We may denote the restoring force in this case by $\beta\Delta$, β being the force-constant now involved which would obviously be different from α . We may describe α as the longitudinal force-constant and β as the transverse force-constant. If we assume the metal and halogen atoms to be held together by chemical bonds along the lines joining them, α would be the force-constant for a stretching of the bonds and β the force-constant arising from a change of the bond-angles. It is evident that if a cube of the crystal is subjected to a hydro-static compression, only the bond-lengths would be altered by the stress and not the bond-angles. If, on the other hand, the cube is subject to a shearing stress, in other words, to tractive forces parallel to its faces, the bond-lengths would remain unaltered but the bond-angles would alter. Thus, in terms of atomic interactions, α is related to the macroscopic stresses arising in a cubic compression, while also in terms of atomic interactions, β is related to the macroscopic forces arising in a pure shear. We shall later make use of this correspondence in seeking to find appropriate values for the force-constants α and β .

The considerations set forth suggest that it should be possible by making use of only the two force-constants α and β and giving them appropriately chosen values, to derive a reasonably satisfactory picture of the dynamics of the atomic vibrations in the alkali halides and hence also of the spectroscopic and thermal behaviour of these crystals. Indeed, it will appear later that this anticipation is justified. However, it would not be correct completely to ignore the interactions arising from the relative displacements of the atoms in the crystal other than the nearest neighbours. Actually, besides the six nearest neighbours situated on the cubic axes, each metal atom has eight halogen atoms located at the corners of the cube of edge length $2d$ at the centre of which it is itself located. Likewise, each halogen atom has eight metal atoms situated in a similar manner with respect to it. The distance between each such pair of metal and halogen atoms is $d\sqrt{3}$, and since this is substantially greater than the distance between adjacent metal and halogen atoms in the crystal, we may assume that the forces arising from their relative displacements would be much less important. There is, however, no difficulty in formally taking them into account in writing down the equations of motion. We may conveniently resolve the relative displacements along each of the three cubic axes, and likewise also resolve the restoring forces along these three axes. Considerations of symmetry indicate that *two* force-constants suffice in all cases to express the ratios of the forces to the displacements. One of them which we shall denote by γ is the ratio of the force to the displacement when they are both parallel to the same cubic axis. The other force-constant relates to the cases

in which the force and the displacement are respectively along two mutually perpendicular cubic axes. Since this force-constant does not actually appear in the equations of motion for any of the nine modes of vibrations with which we are concerned, we shall not trouble to give it a symbol.

Each metal atom in the crystal has also twelve metal atoms as its near neighbours and likewise, each halogen atom has twelve halogen atoms as its neighbours. The line joining each atom with the other similar atoms is of length $d\sqrt{2}$ and is equally inclined to two of the cubic axes and perpendicular to the third. If we proceed on the basis of symmetry considerations alone, it follows that three additional force-constants would be required to express the interaction of the metal atoms with each other and likewise three other constants in the case of the halogen atoms. A considerable simplification however becomes possible when we remark that the distance between the interacting atoms is substantially greater than their common diameter. Hence, the restoring force due to a relative displacement may be expected to be sensible only when this is along their line of join and negligible for a transverse displacement. It follows that the force-constants for a displacement along one of the three cubic axes may be neglected and those which refer to movements along the two other axes would be sensibly equal. Accordingly, only one force-constant which we shall denote by ϕ would be required to express the interactions between the metal atoms, and likewise only one constant which we shall denote by ψ to express those between the halogen atoms.

Summary

It is shown that the restoring forces which arise by reason of the relative displacements of the atoms in the alkali halides during a normal vibration may be expressed by five force-constants which are designated by α , β , γ , ϕ and ψ . The first two are the principal ones and correspond respectively to a stretching of the bonds between adjacent metal and halogen atoms and to a change of the bond-angles. γ is the operative force-constant for relative displacements of metal and halogen atoms separated from each other by a distance $d\sqrt{3}$. ϕ and ψ are the force-constants for the relative displacements of like atoms situated at a distance $d\sqrt{2}$ from each other, ϕ being the constant for the metal atoms and ψ the constant for the halogens.

The specific heats of the alkali halides and their spectroscopic behaviour—Part IV. The equations of motion

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The number and nature of the normal modes of atomic vibration have been discussed in part II of this memoir, while it has been shown in part III that the forces of atomic interaction coming into play during such vibrations may be expressed in terms of five constants, viz., α , β , γ , ϕ and ψ , which between them take account of the interactions between each atom and its twenty-six nearest neighbours in the crystal. Reasons were stated indicating that the most important of them are α and β which express the magnitude of the forces arising when adjacent metal and halogen atoms are displaced with respect to each other respectively along and transverse to the line of their join.

It is now possible to write down and solve the equations of motion for each of the nine normal modes of vibration. It is to be noted that in these modes, the displacements of equivalent atoms appearing in the equations are the same, only their phases being either the same or opposite, and that in each unit cell of the crystal there are only two non-equivalent atoms. The movements of the two species of atoms are coupled with each other in the triply-degenerate principal mode of vibration and also in the four modes of vibration of the atoms appearing in the cubic layers of the structure. Hence, in their cases, we have only two equations of motion which have simultaneously to be solved. But in the four modes of vibration of the octahedral layers, either only the metal atoms or only the halogen atoms oscillate and hence we have only one equation to be written down and solved for each of these four modes. It may also be remarked that in all cases, the *relative* displacements of equivalent atoms are either zero or double their actual displacements according as their phases of vibration are the same or opposite. An important consequence of this is that the frequency of the principal mode of vibration in which the atoms of each species oscillate together is determined only by the three constants α , β and γ , the other two constants, viz., ϕ and ψ not appearing in the equations of motion.

We may denote the masses of the metal and halogen atoms respectively by m_1 and m_2 and the components of their displacements along the three cubic axes respectively by ξ_1, ξ_2 and η_1, η_2 , and ζ_1, ζ_2 . The equations of motions for the principal mode of vibration are accordingly

$$\frac{m_1 d^2 \xi_1}{dt^2} = (2\alpha + 4\beta + 8\gamma)[\xi_2 - \xi_1]$$

$$\frac{m_2 d^2 \xi_2}{dt^2} = (2\alpha + 4\beta + 8\gamma)[\xi_1 - \xi_2]$$

with similar but independent equations for the other two pairs of components. We assume ξ_1 and ξ_2 to be time-periodic and proportional to $\sin \omega_1 t$. Solving the equations, we find that the frequency of the vibration is given by the formula

$$\omega_1^2 = \frac{F}{\mu},$$

where F is an abbreviation for $(2\alpha + 4\beta + 8\gamma)$, and μ is the reduced mass given by the formula

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}.$$

Considering next the oscillations of the metal atoms in the octahedral layers *normally* to those layers and alternating in phase from layer to layer, the relevant equation of motion is

$$\frac{m_1 d^2 \xi_1}{dt^2} = -(F + 16\phi)\xi_1$$

with two similar equations for the displacements η_1 and ζ_1 which appear simultaneously. Accordingly, the frequency of this mode is given by

$$\omega_2^2 = \frac{(F + 16\phi)}{m_1}.$$

The equations for an oscillation of the metal atoms in the octahedral layers in any direction *tangential* to those layers may similarly be written down and solved. The frequency ω_3 of the oscillation is given by the formula

$$\omega_3^2 = \frac{(F + 4\phi)}{m_1}.$$

As is to be expected, the formulae indicate that the vibrations normal to the octahedral layers have the higher frequency. Proceeding similarly, we obtain for the frequencies ω_4 and ω_5 of the oscillations of the halogen atoms in the octahedral layers in directions respectively normal and tangential to those layers,

the expressions

$$\omega_4^2 = \frac{(F + 16\psi)}{m_2}$$

$$\omega_5^2 = \frac{(F + 4\psi)}{m_2}.$$

It will be noticed that the frequencies ω_2 and ω_3 and likewise also ω_4 and ω_5 differ from each other solely by reason of the fact that in these modes, the atoms of the same species oscillate in opposite phases in the successive layers of the structure and hence interact with each other. If the force-constants ϕ and ψ are left out from the expressions for the frequencies, the normal and tangential modes would have identical frequencies and would also be very simply related to each other in the following manner:

$$\omega_1 = \frac{F}{\mu}, \quad \omega_2 = \omega_3 = \frac{F}{m_1}, \quad \omega_4 = \omega_5 = \frac{F}{m_2}.$$

We have next to consider the coupled oscillations of the metal and halogen atoms appearing in the cubic layers of the structure *tangentially* to those layers, the phases alternating from layer to layer. The equations of motion which have simultaneously to be satisfied are

$$\frac{m_1 d^2 \eta_1}{dt^2} = -(F + 8\phi)\eta_1 + (F - 4\beta - 16\gamma)\eta_2$$

$$\frac{m_2 d^2 \eta_2}{dt^2} = (F - 4\beta - 16\gamma)\eta_1 - (F + 8\psi)\eta_2.$$

The frequencies of vibration are given by the pair of roots of the equation obtained by assuming η_1 and η_2 to be time-periodic and eliminating them from the equations. The formula thus obtained is

$$\omega^4 - \omega^2 \Omega_1^2 + \pi_1 = 0$$

where

$$\Omega_1^2 = \left[\frac{(F + 8\phi)}{m_1} + \frac{(F + 8\psi)}{m_2} \right]$$

and

$$\pi_1 = \left[\frac{(F + 8\phi)(F + 8\psi) - (F - 4\beta - 16\gamma)^2}{m_1 m_2} \right].$$

The two roots of this equation are

$$\omega_6^2 = \frac{1}{2} \Omega_1^2 + \left(\frac{1}{4} \Omega_1^4 - \pi_1 \right)^{1/2}$$

$$\omega_7^2 = \frac{1}{2} \Omega_1^2 - \left(\frac{1}{4} \Omega_1^4 - \pi_1 \right)^{1/2}.$$

It is evident that ω_6 would be the higher of the two frequencies. It corresponds to the case in which the metal and halogen atoms in any one cubic layer oscillate in opposite phases; ω_7 , on the other hand, would be the frequency of the vibration in which they oscillate in the same phase, and the restoring forces brought into play are therefore quite small.

Finally, we consider the coupled oscillations of the metal and halogen atoms *normal* to the cubic layers with phases alternating from layer to layer. The equations of motion simultaneously to be satisfied are

$$\frac{m_1 d^2 \xi_1}{dt^2} = -(F + 16\phi)\xi_1 - (F - 8\beta)\xi_2$$

$$\frac{m_2 d^2 \xi_2}{dt^2} = -(F - 8\beta)\xi_1 - (F + 16\psi)\xi_2.$$

Assuming ξ_1 and ξ_2 to be time-periodic and eliminating them from the equations, we obtain the formula

$$\omega^4 - \omega^2 \Omega_2^2 + \pi_2 = 0$$

where

$$\Omega_2^2 = \left[\frac{(F + 16\phi)}{m_1} + \frac{(F + 16\psi)}{m_2} \right]$$

and

$$\pi_2 = \left[\frac{(F + 16\phi)(F + 16\psi) - (F - 8\beta)^2}{m_1 m_2} \right].$$

The two roots of this equation are

$$\omega_8^2 = \frac{1}{2} \Omega_2^2 + \left[\frac{1}{4} \Omega_2^4 - \pi_2 \right]^{1/2}$$

$$\omega_9^2 = \frac{1}{2} \Omega_2^2 - \left[\frac{1}{4} \Omega_2^4 - \pi_2 \right]^{1/2}.$$

It is evident that ω_8 would be greater than ω_9 . The former gives the frequency of the vibration in which the metal and halogen atoms in any cubic layer oscillate in the same phase, while ω_9 is the frequency of a similar vibration in which they oscillate in *opposite* phases. The restoring forces in these modes arise principally from the interactions of the metal and halogen atoms appearing in the adjacent layers.

Comparing the formulae for the four frequencies ω_6 , ω_7 , ω_8 , ω_9 , it is evident that π_2 is greater than π_1 . Hence, these four frequencies when arranged in a descending order of magnitude would appear on the sequence $\omega_6 > \omega_8 > \omega_9 > \omega_7$. This is the order in which the four modes were listed in part II of the memoir.

Summary

Explicit formulae are obtained for the frequencies of the nine normal modes of vibration in terms of the five force-constants α , β , γ , ϕ and ψ . The formulae show that the principal mode in which the metal and halogen atoms oscillate with opposite phases has also the highest frequency of vibration. The formulae also enable the four octahedral modes and the four cubic modes to be arranged amongst themselves in a descending order of frequency.

The specific heats of the alkali halides and their spectroscopic behaviour—Part V. The evaluation of the frequencies

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In the preceding parts of the memoir, it has been shown that the structure of the alkali halides admits of nine distinct species of normal modes of vibration. The geometric characters common to each species were described and their respective degeneracies were deduced. Explicit formulae were also obtained for the vibrational frequency of each of the nine species of normal modes. To achieve the purposes of the memoir, two further steps are necessary. The first is to evaluate the nine frequencies numerically for each of the sixteen halides with which we are concerned. Only when this is done is it possible to proceed to the computation of their specific heats as functions of the temperature. The second step is to discuss the activities of each species of normal vibration in respect of infra-red absorption and reflection as well as in respect of the scattering of light with altered wavelength. This is necessary to enable the observable spectroscopic behaviour of the respective halides to be predicted or interpreted and the theoretically calculated frequencies of the normal modes to be confirmed experimentally.

We proceed to consider the problem of the numerical evaluation of the frequencies of the normal modes of vibration. A knowledge of all the five force-constants, viz., α , β , γ , ϕ and ψ is clearly necessary to enable these computations to be carried out with all necessary accuracy. The question thus arises, how are these constants to be found? A further difficulty arises from the nature of the formulae which have been obtained. These are simple enough in the case of the principal mode of vibration where the frequency is determined by a simple summation ($2\alpha + 4\beta + 8\gamma$) of the first three force-constants. The formulae are also quite simple in the cases of the four octahedral modes of vibration. The force-constants there appearing are also simple summations, viz., ($2\alpha + 4\beta + 8\gamma + 16\phi$), ($2\alpha + 4\beta + 8\gamma + 4\phi$), ($2\alpha + 4\beta + 8\gamma + 16\psi$) and ($2\alpha + 4\beta + 8\gamma + 4\psi$), respectively in the four cases. However, in the case of the four modes of coupled oscillation of the atoms located in the cubic layers, the formulae appear in a much more complicated form involving all the five force-constants combined in different ways in the four cases. The only practicable procedure in these circumstances appears to be that of

making the computations using only the two constants α and β in the first instance and ignoring the other three, viz., γ , ϕ and ψ . The results thus obtained cannot, of course, be strictly correct and would need subsequent amendment, especially in the case of the octahedral modes where the neglect of the force-constants ϕ and ψ would result in making the normal and tangential vibrations of the atoms in the octahedral layers have the same frequencies. Nevertheless, the simplification proposed is substantially justified, since α and β which express the interaction between adjacent metal and halogen atoms due to their relative displacements would obviously be more important than the interactions between atoms which are much further apart. Further, in thus basing the computations on only the two force-constants α and β , we also simplify the question of finding what the force-constants are.

Before we proceed further, it would be useful to present a table giving the description of the nine modes of vibration, their respective degeneracies, and the simplified formulae for their respective frequencies in which only the two force-constants α and β appear. The last column of table 1 gives the expression for $4\pi^2c^2m_h^2v^2$ where c is the velocity of light, m_h is the mass of an atom of hydrogen, m_1 and m_2 now designate the atomic weights of metal and halogen and v is the frequency of the mode expressed in wave-numbers. The modes have been arranged in the table in the descending order of frequency. It should be remarked, however, that if $m_1 > m_2$, the fourth and sixth entries should interchange places in the table, and likewise also the fifth and the seventh entries.

We have now to find a means of ascertaining the magnitudes of the force-constants α and β . As has already been remarked in part III of the memoir, α is the force-constant for a stretching of the chemical bonds which unite the adjacent metal and halogen atoms in the crystal, while β is the force-constant associated with a change of the bond-angles which in the equilibrium state are all right angles. It is evident that if a cube of the crystal is subjected to pressures of equal magnitude normal to all its six faces, in other words to a hydrostatic compression, all the bond-lengths in the crystal would be diminished in the same proportion, but the bond-angles would remain unaltered. Further, if the crystal were subjected to tractive forces parallel to the cube faces, in other words, to shearing stresses, the bond-angles would be altered, but the bond-lengths would remain the same. Thus, macroscopically regarded, the bulk-modulus of elasticity of the crystal bears to its shear-modulus the same relation that α bears to β in an atomistic picture. Hence, we are justified in assuming that α is related in a very simple manner to the bulk-modulus of elasticity and β to the shear-modulus. If we multiply each modulus by the distance d which separates adjacent atoms of metal and halogen, we obtain quantities having the physical dimensions of the force-constants with which we are concerned. Accordingly we proceed to write $\alpha = K \times d$ and $\beta = C_{44} \times d$ where K and C_{44} for each of the alkali halides have the values listed in part I of this memoir.

We may proceed to test the validity of the foregoing expressions for α and β by

Table 1. Simplified frequency formulae

Description of mode	Degeneracy	$4\pi^2c^2m_h^2v^2 =$
Oscillations of the metal and halogen atoms in opposite phases	3	$\frac{(2\alpha + 4\beta)}{\mu}$ or $(2\alpha + 4\beta)\left(\frac{1}{m_1} + \frac{1}{m_2}\right)$
Coupled oscillations in the cubic layers tangentially	6	$\frac{2\alpha + 4\beta}{2\mu} + \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{16\beta(\alpha + \beta)}{m_1m_2}\right]^{1/2}$
Coupled oscillations in the cubic layers normally	3	$\frac{2\alpha + 4\beta}{2\mu} + \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{32\alpha\beta}{m_1m_2}\right]^{1/2}$
Oscillations of the atoms in the octahedral planes normally	4	$\frac{(2\alpha + 4\beta)}{m_1}$
Oscillations of the atoms in the octahedral planes tangentially	8	$\frac{(2\alpha + 4\beta)}{m_1}$
Oscillations of the atoms in the octahedral planes normally	4	$\frac{(2\alpha + 4\beta)}{m_2}$
Oscillations of the atoms in the octahedral planes tangentially	8	$\frac{(2\alpha + 4\beta)}{m_2}$
Coupled oscillations of the atoms in the cubic layers normally	3	$\frac{2\alpha + 4\beta}{2\mu} - \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{32\alpha\beta}{m_1m_2}\right]^{1/2}$
Coupled oscillations of the atoms in the cubic layers tangentially	6	$\frac{2\alpha + 4\beta}{2\mu} - \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{16\beta(\alpha + \beta)}{m_1m_2}\right]^{1/2}$
Translations	3	$v_g \rightarrow 0$

working out their consequences in the case of rock-salt for which the values of all the nine frequencies of vibration of the structure have been determined spectroscopically (reference 1). The bulk-modulus K for rock-salt is 2.52×10^{11} erg/cm³ and the shear-modulus C_{44} is 1.275×10^{11} erg/cm³. Multi-

plying these by d , which is half the lattice-constant and is therefore 2.81 \AA , we find $\alpha = 0.709 \times 10^4 \text{ dyne/cm}$; $\beta = 0.359 \times 10^4 \text{ dyne/cm}$. Using these values of α and β and the simplified formulae for the frequencies of vibration given in table 1 of this part of the memoir, we obtain the following results.

Table 2. Calculated and observed frequencies (in wave-numbers) for NaCl

Degeneracy	3	6	3	4	8	4	8	3	6
Calculated frequencies	187	164	146	146	146	117	117	117	91
Observed frequencies	180	150	129	170	157	140	118	110	92

The highest frequency appearing in table 2 is that of the oscillation of the sodium and chlorine atoms in opposite phases. It is 187 cm^{-1} , which expressed as an infra-red wavelength, comes out as 53.5 microns . Since this mode of vibration is strongly infra-red active, we should expect the maximum reflecting power of a rock-salt surface to be at that wavelength. The rest-strahlen reflections of rock-salt as reported by various observers have a peak at about 54 microns , in excellent agreement with the calculated position. Another satisfactory feature is the close agreement between the calculated and observed values of the eight-fold degenerate frequency (117 cm^{-1}) of the oscillation of the chlorine atoms. This oscillation manifests itself, as is to be expected, in the spectrum of light-scattering by rock-salt as a strong sharp line with the double-frequency shift of 235 cm^{-1} . It is indeed the most conspicuous feature in that spectrum.

In making the calculations, we have ignored the force-constants ϕ and ψ . Since they represent the interactions of like atoms at a distance of $d\sqrt{2}$, their neglect is not wholly justifiable. When they are taken into account, the frequencies which have a four-fold degeneracy would be a little higher than the corresponding frequencies which are eight-fold degenerate. This, it will be seen from table 2, is actually the case for the observed values of the frequencies.

Subject to the foregoing remarks, the agreement between theory and experiment manifested in table 2 may be considered to be highly satisfactory. Accordingly, the same procedure will be adopted in the next part of the memoir in respect of all the other halides.

Summary

Simplified formulae involving only two force-constants α and β are given for the frequencies of the nine normal modes. Reasons are given for identifying the two force-constants as being respectively the products of the bulk-modulus and of the shearing modulus of the crystal by the distance between adjacent metal and

halogen atoms. Calculations made on this basis of the nine frequencies of the rock-salt structure exhibit a highly satisfactory agreement with the spectroscopic data.

Reference

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The specific heats of the alkali halides and their spectroscopic behaviour—Part VI. The atomic vibration spectra

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The preceding parts of this memoir have been devoted to a development of the theory of the vibration spectra of the alkali halides. We have considered the geometry of the free modes of atomic vibration, as also the degeneracies arising from the symmetry of the crystal and shown how the frequencies of vibration may be expressed in terms of certain force-constants and the latter again determined from the elastic moduli of the crystal. The success of the theory was illustrated by reference to the particular case of rock-salt, the behaviour of which is known experimentally. We proceed to consider the cases of all the alkali halides comprehensively, following the same procedures.

The expressions for the frequency of atomic vibration as simplified and tabulated in part V of the memoir contain four quantities which differ from halide to halide, viz., the atomic weights m_1 and m_2 of the metal and halogen atoms respectively and the force-constants α and β . The latter are measures of the restoring forces arising respectively from a longitudinal and a transverse displacement of adjacent metal and halogen atoms in the crystal relatively to each other. As has been shown in the preceding part of the memoir, these force-constants can be equated to the product of the bulk-modulus and the shear-modulus respectively with the distance d between the adjoining metal and halogen atoms in the crystal. The quantity $m_1 m_2 / (m_1 + m_2)$ designated as μ or the reduced mass appears in several of the frequency expressions. Accordingly in table 1, these five quantities, viz., m_1 , m_2 , μ , α , β have been entered in the successive columns of the table for all the sixteen halides.

The following remarks may be made regarding the entries appearing in the table. The reduced mass μ is necessarily smaller than either m_1 or m_2 . When m_1 and m_2 differ greatly, μ approximates pretty closely to whichever of them is the smaller. This is the case for all the lithium halides, as also for the bromide and iodide of sodium and for rubidium fluoride.

The magnitudes of both the force-constants α and β diminish progressively in the sequence of increased atomic weight of the alkali metal as well as of the

Table 1. Atomic weights and force-constants

Substance	m_1	m_2	$\frac{m_1 m_2}{m_1 + m_2}$	α (dynes/cm)	β (dynes/cm)
LiF	6.94	19.0	5.08	1.399×10^4	1.270×10^4
LiCl	6.94	35.5	5.80	0.811×10^4	0.640×10^4
LiBr	6.94	79.9	6.39	0.704×10^4	0.524×10^4
LiI	6.94	127.0	6.58	0.566×10^4	0.405×10^4
NaF	23.0	19.0	10.40	1.121×10^4	0.647×10^4
NaCl	23.0	35.5	13.95	0.709×10^4	0.359×10^4
NaBr	23.0	79.9	17.86	0.625×10^4	0.294×10^4
NaI	23.0	127.0	19.47	0.520×10^4	0.233×10^4
KF	39.1	19.0	12.79	0.849×10^4	0.341×10^4
KCl	39.1	35.5	18.59	0.571×10^4	0.199×10^4
KBr	39.1	79.9	26.25	0.510×10^4	0.168×10^4
KI	39.1	127.0	29.90	0.437×10^4	0.134×10^4
RbF	85.5	19.0	15.55	0.769×10^4	0.256×10^4
RbCl	85.5	35.5	25.07	0.533×10^4	0.156×10^4
RbBr	85.5	79.9	41.30	0.474×10^4	0.132×10^4
RbI	85.5	127.0	51.09	0.407×10^4	0.103×10^4

Table 2. Calculated wave-numbers of the normal modes (in cm^{-1})

Degeneracy	3	6	3	4	8	4	8	3	6
LiF	514	454	450	440	440	266	266	249	241
LiCl	350	326	322	320	320	142	142	137	128
LiBr	305	295	293	293	293	86	86	84	78
LiI	267	261	260	260	260	61	61	60	55
NaF	281	241	210	208	208	189	189	187	144
NaCl	187	164	146	146	146	117	117	117	91
NaBr	152	140	134	134	134	72	72	72	59
NaI	131	124	121	121	121	51	51	51	42
KF	202	182	167	166	166	116	116	114	87
KCl	133	119	102	96	96	92	92	85	60
KBr	105	96	88	86	86	60	60	58	43
KI	90	84	80	79	79	44	44	42	32
RbF	167	158	152	151	151	71	71	69	55
RbCl	103	95	89	87	87	56	56	53	39
RbBr	78	71	63	56	56	54	54	47	33
RbI	64	59	53	49	49	40	40	36	26

halogen. For any particular alkali metal, the force-constants for the fluoride are conspicuously the highest, the differences between the other halides being considerably smaller. A similar situation was remarked for the elastic moduli, but the differences are rather less conspicuous for the force-constants, since the elastic

moduli now appear multiplied by the length d which increases progressively in either of the two sequences.

When we compare the variation of the two force-constants α and β from halide to halide, it is seen that β changes more rapidly than α . Indeed, while α and β are of the same order of magnitude for lithium fluoride, β becomes rapidly the smaller of the two as we go down the table. While β is roughly about one-half of α for sodium chloride, it is only about one-fourth for rubidium iodide.

The results of the calculation of the nine frequencies for all the alkali halides are listed in table 2. The degeneracies entered at the top of the table enable us to identify the different modes. The first entry is that of the triply degenerate oscillation of the metal and halogen atoms against each other in opposite phases. In the case of the other frequencies, a degeneracy of six indicates a coupled oscillation of atoms in the cubic planes tangential to those planes, one of them having the second highest frequency and the other being the lowest. A degeneracy of three indicates a coupled oscillation of the atoms in the cubic planes normal to those planes. It will be noticed that of the two frequencies with this degeneracy, one is much greater than the other. A degeneracy of four indicates the frequency of the oscillations of the atoms in the octahedral layers normal to those layers, while a degeneracy of eight represents the frequency of an oscillation tangential to those layers. These two frequencies for these atoms which have the lower atomic weight are shown first. They are followed by the two frequencies of the atoms with the higher atomic weight.

The very high frequencies of atomic vibration for lithium fluoride are a striking feature of the results of calculation exhibited in table 2. They are a consequence, partly of the low atomic weights of both metal and halogen, and partly of the great strength of the binding between them in this compound. The spectroscopic behaviour of lithium fluoride formed the subject of a recent investigation by the present author (reference 1). The experimental results showed the highest frequency of vibration of the structure to be 508 cm^{-1} which is in gratifyingly close agreement with the theoretically calculated value of 514 cm^{-1} shown in table 2. The nine frequencies lithium fluoride as then found and as of now calculated are exhibited in table 3. The calculated values, being based on the simplified formulae, necessarily differ from the observed values for those modes in which the neglected force-constants ϕ and ψ play a significant role.

A scrutiny of the frequencies for all the halides as calculated and listed in table 2

Table 3. Frequencies of lithium fluoride (in cm^{-1})

Degeneracies	3	6	3	4	8	4	8	3	6
Calculated	514	454	450	440	440	266	266	249	241
Observed	508	417	384	435*	435*	263*	263*	210	210

*Calculated from the observed highest frequency of 508 cm^{-1} .

shows a significant but not unexpected feature, viz., that when the atomic weights of metal and halogen differ greatly, the five highest frequencies form a group which do not differ much from each other and stand apart from the other four frequencies which are much lower. The reason is that the three highest frequencies are those of coupled modes of vibration. When the masses of metal and halogen are very different, the lighter atoms oscillate in the mode of higher frequency while the heavier atoms remain nearly at rest: in the mode of lower frequency, the situation is reversed. Thus, the first five modes listed in the table would have a frequency determined principally or solely by the mass of the lighter atom, while the other four modes would have frequency determined principally or solely by the mass of the heavier atom. As table 2 shows, such a situation arises in the cases of all the lithium halides, sodium bromide, sodium and potassium iodides and rubidium fluoride.

Cases of special interest are those in which the metal and halogen atoms have nearly equal atomic weights, viz., potassium chloride and rubidium bromide. On the basis of the simplified formulae, the oscillations of both species of atoms appearing in the octahedral layers, either normal or tangential to those layers, would have nearly the same frequencies. This situation would be altered when the force-constants ϕ and ψ are taken into account in the calculations. We should nevertheless expect all the four frequencies to approximate to each other and stand apart from those of the modes of higher and lower frequencies.

Finally, we have the cases in which the atomic weights of metal and halogen are neither very close to each other, nor yet very different. The frequencies would then be distributed more or less uniformly over the spectrum instead of being clustered together into groups. Sodium chloride, potassium fluoride and potassium bromide are such cases.

Summary

The frequencies of the nine normal modes of atomic vibration have been tabulated for all the sixteen alkali halides. The results of the calculation are in striking accord with the results of the spectroscopic studies in the two leading cases of lithium fluoride and sodium chloride respectively. The manner in which the structure of the vibration spectra varies with the relative weights of the atoms of metal and halogen is described and discussed.

Reference

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The specific heats of the alkali halides and their spectroscopic behaviour—Part VII. Evaluation of the specific heats

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In seeking to evaluate the thermal energy of a crystal on the basis of the principles of thermodynamics and of the quantum theory, we have to find answers to the following questions: What are the oscillators of which the vibrational energies need to be quantised and totalled up? How can they be identified and enumerated? We shall presently see that the treatment of the problem of the modes of atomic vibration given in the earlier parts of the memoir itself provides the answers to these questions.

We may begin with the case of a simple Bravais lattice. Since each atom in the lattice has 3 degrees of freedom, the general principle that equivalent atoms have the same amplitude while their phases of vibration are either the same or else alternate along one or two or all three axes, results in a simple lattice having 24 possible kinds of movement. Of these, 21 have the character of normal modes of vibration, while the three others are simple translations. In the particular case of a face-centred cubic lattice, the unit cell is a rhombohedron. The total number of degrees of dynamic freedom of movement of the eight atoms located at the corners of this rhombohedron is also 24. Thus, the 21 modes of vibration of the lattice may also be considered as normal modes of vibration of this 8-atom group and its 3 translations as movements of the entire group.

We have seen that the alkali halide structure has nine distinct frequencies of vibration of which the degeneracies are respectively 3, 6, 3, 4, 8, 4, 8, 3 and 6. These add up to a total of 45, or if we include the three omitted translations, to 48. A sixteen-atom group consisting of eight metal and eight halogen atoms linked to each other by chemical bonds would also have 48 degrees of dynamic freedom of movement. Hence, we may appropriately regard such a group as the dynamic unit in the crystal and its nine distinct frequencies of vibration with their characteristic degeneracies as “oscillators” in the specific-heat theory. The three omitted degrees of freedom would be the three translations of the 16-atom group.

It should be remarked that the two cases considered above are only particular examples of a general theorem applicable to all crystals. As has been shown

earlier, if the unit cell of a crystal contains n non-equivalent atoms, the structure of the crystal has $(24n - 3)$ normal modes of vibration. In $(3n - 3)$ of these modes, the vibrations appear in adjacent cells of the lattice with the same amplitudes and phases, while in the $21n$ other modes, the amplitudes of vibration are the same for equivalent atoms but their phases alternate along one, two, or all three axes of the structure. Hence, the *dynamic* unit in the crystal has twice the linear dimensions and hence eight times the volume of the unit cell of its structure. It, therefore, contains $8n$ atoms. The total number of degrees of dynamic freedom of these $8n$ atoms is $24n$. Accordingly, we may describe the $(24n - 3)$ normal modes of vibration of which the structure is capable as the *internal* modes of vibration of the group of $8n$ atoms, while the 3 degrees of freedom not thus accounted for would be the three translations of the group. Thus, the group of $8n$ atoms, or rather each of its frequencies of internal vibration, is identified as the unit oscillator in specific-heat theory, each frequency being counted as many times over as the degeneracy which it may exhibit by reason of the symmetry of the crystal.

One can readily understand why the dynamic unit has twice the linear dimensions and therefore eight times the volume of the static unit in the structure of a crystal. In any normal mode, the vibrations in any one cell would necessarily be coupled with the vibrations in the adjacent cells. In such coupled vibrations, the phases of the vibration in adjacent cells along each axis of the structure may be either the same or opposite. There would thus be eight different possibilities and the vibration frequencies in each of them would necessarily be different. This is the same result as that stated above.

Leaving aside for a moment the translatory movements of the 16-atom groups, we shall consider their internal vibrations. These vibrations appear in the infra-red region of the spectrum and the interatomic forces which determine their frequencies are necessarily strong. But they operate only at short ranges and it may be assumed that they are negligible as between atoms which are further apart from each other than the dimensions of the 16-atom groups. In these circumstances, the internal vibrations of these groups excited by the thermal agitation in the crystal may be expected to be uncorrelated, in other words, to exhibit no coherent relationships of phase as between the different groups. We are accordingly justified in the specific-heat problem in regarding the 16-atom groups as independent oscillators and quantising their energies on that basis.

The thermal energy of the crystal is a summation of the quantised energies of the oscillators of different frequencies included in its volume. There are nine distinct frequencies of vibration, and the number of oscillators having a particular frequency is the same as the number of 16-atom groups contained in the crystal multiplied by the degeneracy of the particular mode. It follows that the Einstein specific-heat function for the particular frequency multiplied by the degeneracy of the mode and divided by 48 gives the contribution of all the oscillators having that frequency to the atomic heat of the crystal. Summing up the contributions

thus made by all the nine frequencies, we obtain the atomic heat of the crystal as a function of the temperature so far as it arises from the spectrum of internal vibrations with discrete frequencies.

We have now to ascertain the contributions to the thermal energy arising from the three translatory movements of the 16-atom groups which we have so far ignored. These translations would necessarily result in displacing the neighbouring atomic groups and hence would set up forces resisting the movement. It follows that the degrees of freedom which do not appear as internal vibrations of the 16-atom groups would manifest themselves as the internal vibrations of atomic groups of larger dimensions. The larger such groups are, the lower would be their possible frequencies of vibration. Hence, the thermal agitation in the crystal associated with the vibrations of specific frequencies already considered would be accompanied by a residual spectrum which by the very nature of the case cannot be expected to exhibit any discrete frequencies and may accordingly be assumed to be continuous and to extend down to very low frequencies.

If the number of 16-atom groups included in the volume of the crystal is N , the total number of degrees of freedom manifested in the residual spectrum would be $3N$. The manner in which the $3N$ degrees are distributed over the range of frequencies covered by that spectrum can be determined by statistical considerations of an elementary nature. We base ourselves on the very reasonable assumption that the lowest frequency of vibration of an atomic group which we denote by ν is inversely proportional to the linear dimensions of the group. On this basis, the volume of each group would be inversely proportional to ν^3 . Consequently, the number of such groups included in the crystal would be directly proportional to ν^3 . Hence, the number of degrees of freedom manifested in the spectral range between ν and $\nu + d\nu$ would be proportional to its differential, viz., $3\nu^2 d\nu$. We assume the spectrum to extend between the lower limit 0 and an upper limit ν_L . Since the total number of degrees of freedom obtained by integration over this range should be $3N$, we obtain the law of distribution to be $3N \cdot 3\nu^2 d\nu / \nu_L^3$. Multiplying this by the Einstein specific-heat function and integrating the product between the limits 0 and ν_L and dividing by 48, we obtain the contribution of the residual spectrum to the atomic heat of the crystal.

Since the residual spectrum represents the frequencies of internal vibration of atomic groups whose dimensions are larger than those of the 16-atom group, ν_L should be of the same order of magnitude as the lowest of its nine discrete frequencies of vibration. We shall not, therefore, be far wrong, at least in the case of the alkali halides, in taking ν_L to be equal to the lowest of the nine discrete frequencies.

Of the total number of degrees of atomic freedom, only one-sixteenth part appears in the residual spectrum of frequencies. The largest part of this again is concentrated near the upper limit of that spectrum by reason of the law of distribution of frequencies in it. Indeed, only 1/128th part of the total number of degrees of atomic freedom would be left not accounted for if we omitted to

consider vibrations in volume elements whose linear dimensions are greater than twice the dimensions of the 16-atom groups having discrete frequencies of vibration. Thus, in the evaluation of the thermal energy of the crystal, we are concerned almost exclusively with vibrations localised in extremely small elements of volume in the crystal. We shall not be seriously in error in assuming such oscillations to be uncorrelated in phase as between different elements of volume and hence permitting of being quantised independently of each other.

Summary

The determination of the normal modes of atomic vibration in the earlier parts of the memoir also enables us to identify and enumerate the oscillators of which the quantised energies of vibration constitute the thermal energy of the crystal. Besides the oscillators with the nine discrete frequencies, there are others which give rise to a residual spectrum of vibrations with lower frequencies. The distribution of frequencies in that spectrum is determined and its contribution to the thermal energy is evaluated.

The specific heats of the alkali halides and their spectroscopic behaviour—Part VIII. Their infra-red activity

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The alkali halides play a highly important role in infra-red spectroscopy. Dispersing prisms of large size fashioned from synthetically prepared crystals of optical quality are made use in the recording infra-red spectrophotometers currently in use. The dispersive power of the materials in the spectral regions of free transmission, the absorption which they exhibit further out in the infra-red and the intense surface reflections by them observable at still greater wavelengths are thus matters of particular interest and importance. We shall proceed to consider these topics in relation to the subject-matter of the earlier parts of the memoir, viz., the free modes of atomic vibration possessing discrete frequencies in the region of the infra-red.

We may begin with some comments on the general nature of the relationship which we shall consider presently in greater detail. The specific heats of crystals and their infra-red activity deal with matters which may at first sight seem wholly unrelated to each other. The heat energy of a crystal is identifiable with the mechanical energy of vibration of the massive nuclei of the atoms carrying positive charges about their positions of equilibrium. The infra-red activity of a crystal, on the other hand, is ascribable to the movements of the negatively charged electronic clouds induced by the field of the incident radiation. That there is a connection between these subjects is a consequence of the fact that the atomic nuclei in a crystal are held in their places by the negatively charged electronic clouds and vice versa. In appropriate circumstances, but not necessarily in every case, an oscillation of the atomic nuclei may be accompanied by periodic displacements of the negatively charged electronic clouds, and vice versa.

Infra-red activity implies the possibility of a transference of the energy of the incident radiation to the crystal. If such transference actually occurs, the incident radiation is absorbed, the quanta of its energy being taken over and transformed into one, two or more quanta of vibrational energy in the crystal. If, on the other hand, the transference is only virtual, the velocity of propagation of the electromagnetic waves is influenced and we have free transmission but with an

altered velocity. In appropriate circumstances also, the response of the crystal to the field may be so great that the incident energy is returned to the external medium, in which case we observe a powerful reflection.

The part which the positively-charged massive atomic nuclei and the negatively charged electrons respectively play in the infra-red activity of crystals may next be considered. As has been shown in the preceding parts of the memoir, the discrete frequencies of atomic vibration are determined by the specific modes of such vibration, by the masses of the atomic nuclei, and by the interatomic forces. The latter arise by virtue of the metal and halogen atoms being held together by the bonding electrons. The displacements of electric charge which are responsible for the absorption, dispersion and reflection of infra-red radiation are solely due to the movements of the negatively charged electrons, the movements of the positive charges represented by the atomic nuclei making no contribution to it. To make this point obvious, we have only to recall the infra-red behaviour of crystals such as quartz and rock-salt. In these crystals, the nuclear masses bear to each other the same ratio as the positive charges which they carry. Since in every one of the modes of atomic vibration, the centres of inertia of the oscillating units remain at rest, the centres of positive charge also remain undisturbed in any such oscillation.

If each of the atomic nuclei has around it a spherically symmetrical distribution of negative charge equal and opposite to the positive charge of the nucleus and if further, this situation is not sensibly altered by a movement of the nuclei, there could evidently be no infra-red activity. Actually, the alkali halides display a powerful infra-red activity. It is also well known that their dielectric constants as determined with periodically varying electric fields of low frequency are notably higher than the square of their refractive indices in the visible region of the spectrum. The data for all the sixteen halides are exhibited in table 1.

Table 1. Dielectric constants of the alkali halides*

	Fluoride	Chloride	Bromide	Iodide
Lithium	9.27	11.05	12.1	11.03
Sodium	6.00	5.62	5.99	6.60
Potassium	6.05	4.64	4.78	4.94
Rubidium	5.91	5.0	5.0	5.0

*From table in *American Institute of Physics Handbook*, 1957.

The dielectric behaviour of the alkali halides as set out in table 1 exhibits some significant features. It is obviously unrelated to the strength of the binding between the metal and halogen atoms. The latter exhibits large variations as is indicated by the elastic moduli and the frequencies of atomic vibration of the various halides. The variations of dielectric behaviour are altogether of a different

character. The dielectric constant is highest when the metal and halogen atoms differ greatly in their sizes. It is low when the two sets of atoms are of comparable dimensions. The former situation is exemplified by the lithium halides and the latter by potassium chloride. These show respectively the highest and lowest dielectric constants listed in table 1.

An explanation of the facts which suggests itself is that an external electric field produces a displacement of the negatively charged electronic cloud located between each pair of metal and halogen atoms in the crystal. Such a displacement may be expected to be comparatively small when the metal and halogen atoms are nearly of the same dimensions and distinctly large when they are very different. A similar explanation would account for the infra-red activity exhibited by the alkali halides. Indeed, such activity could only be explained on the basis that the field of the incident radiation induces a periodic displacement of the negatively charged cloud of electrons in the crystal.

On the basis of the ideas set forth above, one can proceed to draw inferences regarding the infra-red activity of the nine characteristic modes of vibration of the alkali halides. A periodic displacement of negative electric charge which does not vanish when summed up over the volume of the oscillating unit is essential for any particular mode of vibration to exhibit activity. The magnitude of the displacement of charge is also a measure of the strength of such activity. It follows that the mode of vibration of the highest frequency in which the metal and halogen atoms oscillate against each other in opposite phases would be powerfully active. For, the phases of the oscillation being the same in successive cells of the structure, their effects would add up.

Altogether different would be the behaviour of the oscillations of the atoms located in the octahedral layers of the structure. There are four modes of this kind, *only* the metal atoms oscillating in two of them and *only* the halogen atoms in the two others, the movements being respectively normal and tangential to those layers. Since in each of the modes the phase of the oscillation is reversed as we pass from layer to layer, the displacements of negative charge resulting therefrom would cancel each other completely. In other words, these four modes would be totally inactive.

The coupled oscillations of the metal and halogen atoms appearing in the cubic layers may next be considered. Since adjacent metal and halogen atoms in the structure alternately approach and recede from each other, there would be a resulting displacement of negative charge. But since the phases are reversed in the successive layers of the structure, they would cancel out when summed up over the volume of the oscillating unit. But in the second approximation when the amplitudes of vibration are not infinitesimal, the cancellation would not be complete, and there would be a surviving component of charge displacement which has a doubled frequency. In other words, these four modes which are inactive in the first approximation would be active as overtones, the radiation being absorbed when it has twice the frequency of the mode. It should be

remarked that the four modes would display such activity with very different strengths. The two having the higher frequencies should, for fairly obvious reasons, be much more strongly active than the two others.

As was remarked earlier, when the radiation is absorbed, its energy quanta are taken up and transformed into one, two or more quanta of vibrational energy in the crystal. The frequency of the absorbed radiation would then be a multiple of the frequency of vibration of the structure. The circumstances in which such absorption may be expected to occur are of importance. It is clear that the absorption of radiation with frequencies which are overtones of the frequencies of atomic vibration would only be possible when the oscillations are of large amplitude and there is an appreciable anharmonicity, a situation that could only arise when the oscillating unit is itself not of any large dimensions.

The mode of vibration having the highest frequency is also the most strongly active, viz., that in which the metal and halogen atoms oscillate in opposite phases. It is, therefore, to be expected that this mode would exhibit the absorptions of higher orders in which the frequency of the absorbed radiation is a multiple of its own frequency. Their strength would naturally fall off rapidly with the increasing order of absorption. Hence, the absorption paths necessary to exhibit them would progressively become greater. Experimental studies with MgO, rock-salt and lithium fluoride¹⁻³ completely substantiate this inference.

The absorptions of higher order determine the upper limit of wavelength beyond which the alkali halides are not sufficiently transparent for use as dispersing prisms. This limit is about 15 microns for NaCl, 21 microns for KCl, 27 microns for KBr and 31 microns for KI. These figures may be compared with the infra-red wavelengths which correspond to the highest atomic vibration frequencies. For the four halides mentioned, they are respectively 53 microns, 75 microns, 95 microns and 111 microns; in each case, these wavelengths are between three and four times greater than the limits mentioned. It is clear that the third-order absorption by the alkali halides is of considerable strength and that not until it has disappeared and given place to the much weaker fourth-order absorption is the material sufficiently transparent for use as a dispersing prism.

The possession of an adequate dispersive power is essential for the satisfactory performance of its functions by a dispersing prism. All the four halides mentioned, viz., NaCl, KCl, KBr and KI have very small dispersive powers in the near infra-red, in other words in the wavelength range between one micron and five microns. In this range, therefore, prisms of the materials mentioned cannot be usefully employed. The dispersive power of NaCl reaches satisfactory values beyond 8 microns, that of KCl beyond 10 microns, that of KBr beyond 15 microns and that of KI beyond 20 microns. The experimental data exhibit a significant parallelism between the increases of the absorption coefficient and of the dispersive powers with increasing wavelength. The useful range is thus set at one end by the dispersive power being too small and at the other end by the absorption being too great.

The mechanism of infra-red activity discussed in the foregoing pages lends itself to a very simple explanation of the well known phenomenon of the surface reflections exhibited by the alkali halides. The incidence of radiation on the crystal would result in a periodic displacement of negative electric charge in each unit cell of the structure. Since the displacements in all the cells have a coherent phase-relationship, their effects would be additive and hence could give rise to a reflected wave-front, the strength of such reflection being proportional to the strength of the electric displacements induced by the field. An effect of this nature would *not* necessarily be limited to the particular cases in which the incident radiation has the same or nearly the same frequency as the most strongly active mode of atomic vibration. It should also be observable in other circumstances and especially when the frequency of the incident radiation approximates to that of the other modes of free atomic vibration and/or their overtones.

Lithium fluoride furnishes a very striking illustration of the foregoing remarks. The manner in which the intensity of the surface reflections by that crystal varies with the wavelength of the incident radiation has been described and discussed in the memoir dealing with it. Magnesium oxide and rock-salt also show distinctive features in their reflection spectra. These have been described and adequately discussed in the memoirs dealing with those materials. There is, therefore, no need to traverse the same ground here again in detail.

Summary

The dispersion, absorption and reflection of infra-red radiation by the alkali halides receive a satisfactory explanation as consequences of the electric field of the incident radiation inducing a periodic displacement of the negative electric charges located between each pair of metal and halogen atoms in the crystal. The dielectric behaviour also receives an acceptable interpretation on the same basis. The appearance of infra-red absorption at wavelengths corresponding to the overtones of the frequencies of atomic vibration indicates that the oscillating units in the crystal have dimensions comparable with those of the unit cells.

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The specific heats of the alkali halides and their spectroscopic behaviour—Part IX. Spectral shifts in light scattering

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The dynamical theory which enabled the evaluation of the thermal energy of the alkali halides was also the basis for the discussion of their infra-red activity contained in the preceding part of the memoir. But there is a great difference between the two problems; whereas all the nine modes of vibration are excited by the thermal agitation to extents determined by their frequencies and the temperature, the infra-red activities of the different modes are determined by totally different considerations. Some are wholly inactive and some others are active only in the higher orders. In consequence, rather elaborate studies with absorption paths ranging from large down to the smallest values in the different spectral ranges are necessary to enable any useful conclusions to be drawn regarding the character of the vibration spectrum in each particular case. Further, the characteristic frequencies for most of the alkali halides lie in the remote infra-red far beyond the range of the recording spectrographs provided with NaCl and KBr optics.

From the foregoing remarks, it is evident that for a complete determination of the modes and frequencies of atomic vibration in the alkali halides, we have of necessity to rely upon methods of observation other than those of infra-red spectroscopy. Since the alkali halides are transparent both in the visible and in the ultra-violet regions of the spectrum, one naturally turns to the application of the methods based on the spectroscopic examination of the radiations scattered in the crystal when traversed by a powerful beam of monochromatic light. Actually, however, the earlier attempts made with rock-salt to record the spectral shifts of frequency usually noticeable in such circumstances did not prove successful. The reason for this failure is not far to seek. It is to be found in the nature of the modes of atomic vibration when considered in relation to the structure of the crystal. We shall comment on these matters in some detail as this will lead us to a clearer understanding of the circumstances in which positive results can be expected as well as the nature of such results.

The nine possible modes of vibration of the structure of the alkali halides differ from each other both in the geometry of the movements and in their frequencies. But they exhibit certain features in common arising from the cubic symmetry of the structure. The principal mode of vibration of the highest frequency and the four modes of vibration of the atoms appearing in the cubic layers may all be described as an approach of each atom of one species towards an atom of the other species on one side of it and a recession from a similar atom on the other side, these movements being reversed in the successive half-periods of the oscillation. The four octahedral modes in which only the atoms of one species oscillate and the atoms of the other species remain at rest are of a different character. Each moving atom of one species approaches a group of atoms of the second species on one side of it and recedes from a similar group lying on the other side and these movements are reversed in the successive half-periods of the oscillation. The group of stationary atoms consists of three atoms for the perpendicular modes and of two atoms for the tangential ones.

The spectral shifts of frequency recorded in the scattering of light are a consequence of the periodic changes in the optical polarisability of the oscillating groups of atoms resulting from their internal vibrations. These changes are a summation of the changes produced by the approaches and recessions of the individual atoms during their movements. From the description of the modes of vibration given above, it is evident that in all the nine cases, the result of the summations would be zero in the first approximation but finite in the second approximation, the magnitude of the resultant being naturally very different for the different modes. The vanishing result of the summation in the first approximation is a consequence of the effects produced by the approaches on one side being cancelled out by the effects due to the recessions on the other side; since the movements are of equal amplitude, the effects arising therefrom may be assumed to be equal in magnitude but opposite in sign. The assumption is a reasonable one provided the movements are of infinitesimal amplitude. But it ceases to be valid if the amplitudes are not small, and hence in the second approximation, the summation would give a finite result and this would evidently be periodic with twice the frequency of the oscillation.

Thus we arrive at the result that spectral shifts of the first-order, in other words, changes of frequency identical with those of the modes of vibration would fail to manifest themselves when a beam of monochromatic light traverses a crystal of the alkali halides and the scattered radiation is examined spectroscopically. The possibility of spectral shifts of doubled frequency is however indicated by the argument. For such shifts to be observable, there are two prerequisites. In the first place, the optical polarisabilities should themselves be of sufficient magnitude so that any changes thereof could produce sensible effects. Secondly, the amplitudes of vibration of the oscillating units should be sufficiently large so that the second-order effects due to optical anharmonicity may be observable. Since the energy of mechanical vibration is quantised and therefore determined by the frequency and

not by the dimensions of the oscillators, amplitudes of oscillation of a magnitude comparable with the dimensions of the individual atoms are only possible if the oscillator is itself not of very large dimensions, in other words, is a group of atoms comparable in its size with the dimensions of the unit cell of the crystal. Thus, the observability of spectral shifts with doubled frequency may be regarded as a demonstration that the oscillators in the crystal are sufficiently small to exhibit the effects of optical anharmonicity.

The spectral shifts of doubled frequency would be both positive and negative, in other words, would appear on both sides of the exciting radiation in the spectrum, the ratio of their intensities being the ratio of the numbers of the thermally excited to the non-excited vibrational states. This ratio also figures in specific heat theory. Thus, the observable features in the spectra of light scattering of the alkali halides all stand in the closest relationship to the dynamical theory developed in the earlier parts of the memoir. All the nine modes of atomic vibration would appear with doubled frequency shifts though necessarily with very different intensities, thereby making it possible to obtain a complete observational proof of the theory on which the evaluation of the specific heats was based.

We now turn to a consideration of the circumstances which would favour the spectral shifts of doubled frequency being recorded with observable intensities. It is obvious that the light beam traversing the crystal should be of great intensity. This, however, may result in various spurious effects of instrumental origin. Thus, unless the crystal is itself highly transparent and non-luminescent, a successful recording of the second-order spectrum could scarcely be hoped for.

As can be seen from the tabulated values in the first part of this memoir, the fluorides of all the alkali metals have very low refractive indices. Hence, one could scarcely hope to record the second-order spectra successfully with them. The refractive indices of the chlorides, bromides and iodides of all the alkali metals are much greater, particularly those of the iodides. They are, therefore, much more promising material for the studies.

The spectral shifts of frequency would be greatest in the case of the lithium compounds and smaller for those of the other alkali metals. The shifts in each case would be smaller for the bromides and iodides than for the chlorides. The smaller frequency shifts would be recorded in closer proximity to the exciting radiation in the spectrum. In the vicinity of the latter, various spurious effects are inevitable, e.g., ghosts and continuous spectrum. Unless the presence of such spurious effects is recognised and allowed for, erroneous interpretations of the observed results are possible.

For the interpretation and evaluation of the recorded spectra, a comparison with the theoretically expected frequency shifts and especially their relative intensities should obviously be helpful. These intensities are determined by two considerations, viz., the geometry of the vibrational modes and their degeneracies. Those modes of vibration in which adjoining metal and halogen atoms

do not approach each other closely and hence cannot strongly influence each other's optical polarisabilities could only be recorded very feebly. This is illustrated by the two modes of vibration of the lowest frequencies of the atoms appearing in the cubic layers. These modes are necessarily also the modes exhibiting the lowest recorded intensities in the spectra.

It was remarked in the preceding part of the memoir that the four modes of vibration of the octahedral layers of atoms are totally inactive in the absorption of infra-red radiation. It is, therefore, a particularly valuable feature of the spectra of light scattering that all these four modes can appear in them with doubled frequency shifts. In particular, the two tangential modes of vibration of the octahedral layers may be expected to appear with high intensities by reason of their degeneracy being eightfold. Indeed, they might well be the most conspicuous features in the spectra in all cases.

The support which the results of studies of light scattering in the alkali halides give to the theory of their specific heats set out in the present memoir is strikingly illustrated by the case of rock-salt. In the memoir dealing with the spectroscopic behaviour of this crystal¹ the microphotometer record of the spectrum of light scattering in it obtained by Rasetti with the special technique developed by him was reproduced. It was shown that the record exhibits a highly satisfactory agreement with the consequences of the theory. All the nine frequency shifts expected on the basis of the theory appear in the positions and with the relative intensities indicated by it.

We may conclude this part of the memoir with some comments on the spectroscopic behaviour of the alkali halides as manifested respectively in light-scattering and infra-red absorption. The alkali halides are extremely powerful absorbers of infra-red radiation in the appropriate wavelength ranges. Far from this being a helpful circumstance, it is actually an embarrassing feature. The absorption arises from the movements of the negative charges in the crystal set up by the electromagnetic field of the incident radiation. These movements react with the field and result in the observed absorption. The moving charges are the bonding electrons located between the metal and halogen atoms in the crystal. The atomic nuclei and the electrons surrounding them are also disturbed in consequence, but the role played by their movements is a purely subordinate one. It is not to be expected in these circumstances that infra-red absorption studies could fully reveal the real characters of the atomic vibration spectrum.

On the other hand, the scattering of light is a feeble effect and this is a helpful feature, since the various complications which arise in the infra-red investigations are thereby excluded. The spectral shifts of frequency in the scattering of light are a consequence of the localised periodic variations of optical polarisability in the structure due to its vibrations. All the electrons surrounding each atomic nucleus contribute to the optical polarisability of the structure. Hence the movements of the atomic nuclei control the magnitude and character of the variations of optical polarisability. Accordingly, we would be justified in expecting that the spectrum

of light scattering would be a more or less faithful representation of the atomic vibration spectrum and would enable the real character of the latter as a set of discrete frequencies to be recognised.

Summary

The spectral shifts of doubled frequencies observed in the scattering of light by the alkali halides—rock-salt for example—are discussed and explained and it is shown that they demonstrate the validity of the approach to the theory of their specific heats developed in the present memoir.

Reference

1. Raman C V *Proc. Indian Acad. Sci.* **A54** 253–304 (1961).

The specific heats of the alkali halides and their spectroscopic behaviour—Part X. The lithium salts

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A distinguishing feature of the lithium halides is the great disparity between the atomic weights of the metal and halogen atoms which are their constituent elements. Noteworthy also is the strength of the chemical bonds holding the structure together which is indicated by the magnitudes of the force-constants. As a consequence of these features, five of the atomic vibration frequencies have high values, while the other four frequencies are much lower. The vibration spectrum thus consists of two distinct sectors. This is reflected in the thermal behaviour of the crystals. The atomic heat rises rather steeply in the lower ranges of temperature, and this is followed by a much less rapid increase towards the limiting value at higher temperatures.

The manner of computation of the atomic heats has already been explained in part VII of this memoir. The computation is based on the frequencies of the free modes of atomic vibration and their respective degeneracies. The frequencies now made use of for each case are shown in table 1 below. The details of the

Table 1. Atomic vibration frequencies (in cm^{-1})

	Degeneracies								
	3	6	3	4	8	4	8	3	6
LiF	508	417	384	435	435	263	263	210	210
LiCl	367	343	336	336	336	148	148	147	130
LiBr	325	315	312	312	312	92	92	92	80
LiI	280	274	273	273	273	64	64	64	56

computation are set out in tables 2, 3, 4 and 5 appearing in the succeeding pages. The results have been graphically represented as functions of the absolute temperature in figures 1 and 2 appearing below in the text. Figure 2 exhibits the computed atomic heats for all the four halides to facilitate their comparison with each other.

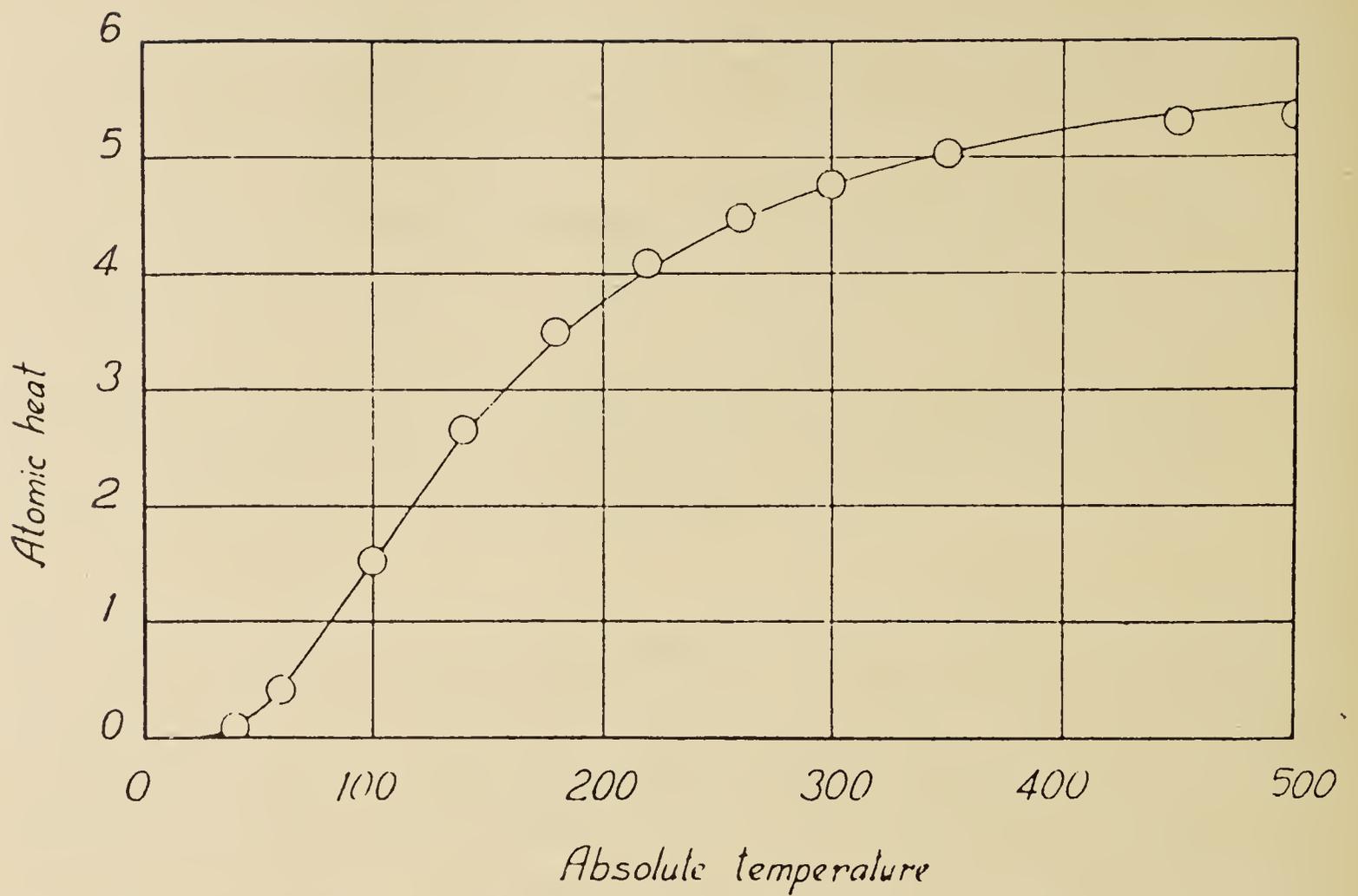


Figure 1. Atomic heats of lithium fluoride. Computed values———. Observed values ○ ○ ○ ○.

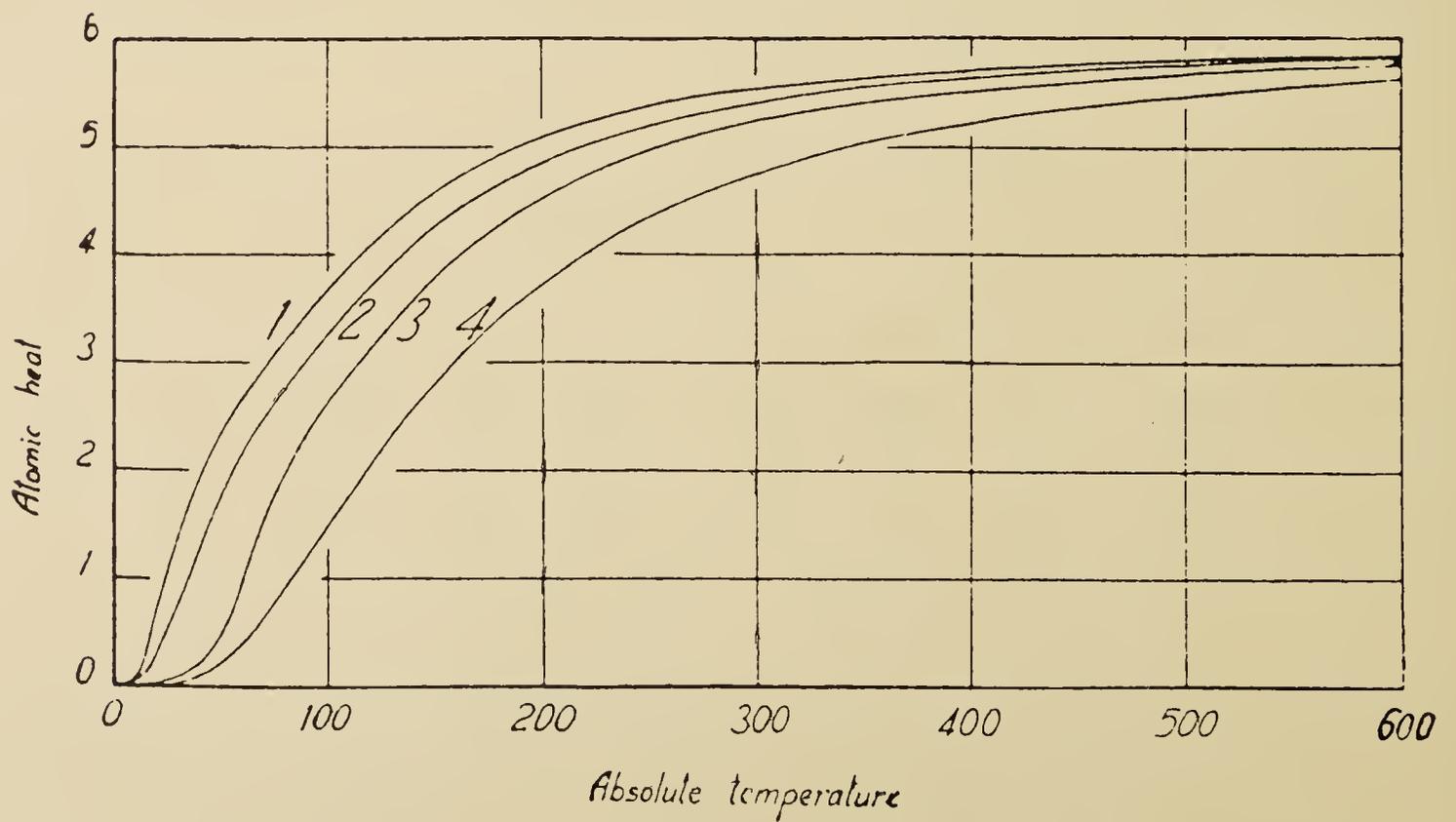


Figure 2. Computed atomic heats of (1) LiI, (2) LiBr, (3) LiCl, (4) LiF.

Neither spectroscopic studies nor any measurements of specific heats have been reported for lithium chloride, lithium bromide and lithium iodide. The only specific heat data available are those for lithium fluoride. The spectroscopic behaviour of lithium fluoride in the infra-red has been the subject of a detailed investigation by the present author¹. The characteristic frequencies determined from that investigation have been shown in table 1 and made use of in the computations set out in table 2. The experimental values have been plotted in figure 1 in order to exhibit the agreement of the experimental data with the theoretical computations.

The highest frequency of 508 cm^{-1} appearing in table 1 is precisely determined from the spectrophotometer records of absorption by the thinnest cleavage plates of lithium fluoride which exhibit a very pronounced and sharply defined absorption maximum at $9.84\ \mu$, the wavelength corresponding to the octave of that frequency. The frequencies of 435 cm^{-1} and 263 cm^{-1} of the inactive octahedral modes were deduced from the frequency of 508 cm^{-1} by a simple calculation based on the individual masses of the lithium and fluorine atoms respectively as compared with the reduced mass which determines the highest frequency. The frequencies of the four active cubic modes 417 cm^{-1} , 384 cm^{-1} , 210 cm^{-1} , 210 cm^{-1} are observational values derived from the spectrophotometer records which exhibit the absorptions of the second order due to the corresponding modes. Thus, the computations are based exclusively on the spectroscopic observations. In the circumstances, the agreement of the computed results with the observed thermal behaviour over the entire range of temperature exhibited in figure 1 forms an impressive demonstration of the validity of the ideas on which the computations are based.

It will be noticed from table 1 that the atomic vibration frequencies listed in it fall into two groups. The frequencies in each group differ but little from each other, and indeed in the cases of lithium bromide and lithium iodide, they are practically identical. The frequencies of both the groups diminish with the increasing atomic weight of the halogen, the fall being proportionately more rapid for the second group. As a consequence, the atomic heats of the lithium halides exhibit their greatest differences in the lower ranges of temperature.

It would obviously not be quite correct to base the computations of the atomic heat at low temperatures on the atomic vibration frequencies as determined by spectroscopic observations made at room temperature, since they would be a little different at the lower temperatures. Likewise, it would not be strictly correct to make use of the elastic constants measured at room temperatures for a computation of the atomic vibration frequencies effective at low temperatures. Hence, certain corrections are necessary. Their magnitudes are not the same in all the cases. They are small enough to be ignored in the case of LiF, but are sensible for the three other halides. The necessary corrections to the vibration frequencies have been made in table 1.

Table 2. Computation of the atomic heats of lithium fluoride

Temperature	20° K	40° K	60° K	100° K	140° K	180° K	220° K	260° K	300° K	350° K	400° K	450° K	500° K
3E(508)	—	—	0.0003	0.0124	0.0530	0.1061	0.1559	0.1971	0.2293	0.2594	0.2821	0.2982	0.3112
12E(435)	—	0.0001	0.0042	0.1054	0.3368	0.5773	0.7784	0.9275	1.0377	1.1417	1.2116	1.2653	1.3036
6E(417)	—	—	0.0030	0.0633	0.1868	0.3104	0.4074	0.4811	0.5342	0.5821	0.6165	0.6412	0.6578
3E(384)	—	0.0001	0.0028	0.0435	0.1133	0.1760	0.2224	0.2568	0.2805	0.3021	0.3171	0.3277	0.3362
12E(263)	—	0.0094	0.1025	0.4932	0.8250	1.0342	1.1642	1.2449	1.3013	1.3508	1.3798	1.4025	1.4178
9E(210)	0.0001	0.0309	0.1782	0.5398	0.7603	0.8828	0.9533	0.9948	1.0254	1.0474	1.0633	1.0748	1.0830
3D(210)	0.0081	0.0574	0.1325	0.2430	0.2966	0.3236	0.3387	0.3476	0.3536	0.3582	0.3614	0.3638	0.3655
Calc. C_v	0.0082	0.0979	0.4235	1.5006	2.5718	3.4104	4.0203	4.4498	4.7620	5.0417	5.2318	5.3735	5.4751
Exptl. C_v *	0.0086	0.1030	0.4110	1.5250	2.6650	3.5080	4.0760	4.4580	4.7724	5.0245	5.1908	5.2951	5.3496

* (1) Clusius K, Goldmann J and Perlick A Z. *Naturforschung*, **A4**, 424-32 (1949).

(2) Douglas T B and Denver J L J. *Am. Chem. Soc.*, **76**, 4826-29 (1954).

Table 3. Computation of the atomic heats of lithium chloride

	25° K	50° K	75° K	100° K	100° K	200° K	250° K	300° K	350° K	400° K	450° K	500° K	550° K	600° K
3E(367)	—	0.0009	0.0151	0.0511	0.1415	0.2113	0.2577	0.2879	0.3075	0.3213	0.3308	0.3392	0.3444	0.3486
6E(343)	—	0.0063	0.0422	0.1271	0.3164	0.4534	0.5393	0.5932	0.6297	0.6542	0.6739	0.6856	0.6952	0.7033
15E(336)	—	0.0097	0.1153	0.3378	0.8175	0.1550	1.3649	1.4988	1.5853	1.6414	1.6910	1.7194	1.7431	1.7606
15E(148)	0.0246	0.4750	0.9729	1.2799	1.5707	1.6936	1.7506	1.7831	1.8030	1.8168	1.8263	1.8333	1.8388	1.8429
6E(130)	0.0217	0.2531	0.4482	0.5560	0.6530	0.6909	0.7098	0.7204	0.7267	0.7311	0.7339	0.7361	0.7382	0.7393
3D(130)	0.0587	0.1992	0.2759	0.3129	0.3443	0.3560	0.3617	0.3650	0.3669	0.3682	0.3690	0.3696	0.3701	0.3704
Calc. C_v	0.1050	0.9412	1.8696	2.6648	3.8434	4.5602	4.9840	5.2484	5.4191	5.5330	5.6249	5.6832	5.7298	5.7651

Table 4. Computation of the atomic heats of lithium bromide

	25° K	50° K	75° K	100° K	150° K	200° K	250° K	300° K	350° K	400° K	450° K	500° K	550° K	600° K
3E(325)	—	0.0025	0.0269	0.0744	0.1720	0.2379	0.2780	0.3037	0.3206	0.3308	0.3403	0.3455	0.3501	0.3536
6E(316)	—	0.0064	0.0611	0.1615	0.3599	0.4880	0.5659	0.6149	0.6468	0.6678	0.6836	0.6941	0.7023	0.7089
15E(312)	—	0.0173	0.1593	0.4161	0.9115	1.2286	1.4230	1.5411	1.6206	1.6732	1.7115	1.7380	1.7581	1.7744
15E(92)	0.2521	1.0566	1.4353	1.6065	1.7431	1.7933	1.8168	1.8305	1.8402	1.8456	1.8509	1.8523	1.8536	1.8544
6E(80)	0.1550	0.4828	0.6104	0.6647	0.7080	0.7241	0.7311	0.7355	0.7388	0.7406	0.7411	0.7416	0.7420	0.7423
3D(80)	0.1525	0.2881	0.3306	0.3480	0.3612	0.3661	0.3682	0.3694	0.3702	0.3707	0.3710	0.3713	0.3715	0.3716
Calc. C _v	0.5596	1.8537	2.6236	3.2712	4.2557	4.8380	5.1830	5.3951	5.5372	5.6287	5.6984	5.7428	5.7776	5.8052

Table 5. Computation of the atomic heats of lithium iodide

	25° K	50° K	75° K	100° K	150° K	200° K	250° K	300° K	350° K	400° K	450° K	500° K	550° K	600° K
3E(280)	—	0.0070	0.0480	0.1085	0.2079	0.2662	0.2998	0.3199	0.3324	0.3418	0.3476	0.3521	0.3558	0.3583
6E(274)	—	0.0161	0.1034	0.2265	0.4261	0.5393	0.6043	0.6440	0.6693	0.6856	0.6973	0.7063	0.7124	0.7173
15E(273)	0.0001	0.0409	0.2618	0.5724	1.0650	1.3523	1.5144	1.6100	1.6732	1.7141	1.7431	1.7656	1.7831	1.7953
15E(64)	0.6526	1.4024	1.6384	1.7327	1.8030	1.8277	1.8415	1.8496	1.8523	1.8540	1.8549	1.8557	1.8564	1.8568
6E(56)	0.3270	0.5995	0.6764	0.7043	0.7267	0.7344	0.7388	0.7409	0.7416	0.7421	0.7424	0.7427	0.7429	0.7430
3D(56)	0.2301	0.3272	0.3511	0.3600	0.3669	0.3692	0.3702	0.3709	0.3713	0.3716	0.3717	0.3718	0.3718	0.3719
Calc. C _v	1.2098	2.2931	3.0791	3.7044	4.5956	5.0891	5.3690	5.5353	5.6401	5.7092	5.7570	5.7942	5.8224	5.8426

Summary

The great disparity between the atomic weights of the constituent metal and halogen atoms has a notable influence on the character of the vibration spectra as also on the thermal behaviour of the lithium halides. The atomic heat rises rather steeply in the lower ranges of temperature and this is followed by a relatively slow increase towards the limiting value at higher temperatures.

Reference

1. Raman C V *Proc. Indian Acad. Sci.* **A55** 133 (1962).

The specific heats of the alkali halides and their spectroscopic behaviour—Part XI. The sodium salts

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The atomic vibration spectra of all the alkali halides, each consisting of a set of nine discrete frequencies, were computed and listed in part VI of this memoir. The calculations which were made took into account the two force-constants α and β expressing the interactions between adjoining metal and halogen atoms in the structure. α and β refer respectively to the longitudinal and transverse displacements of the two atoms relative to each other and are very simply related to the bulk-modulus and shear-modulus respectively of the crystal. They are, therefore, readily evaluated from the results of ultrasonic measurements of the elastic constants.

In the case of the four sodium halides, the highest of the nine frequencies expressed as a wave-number, came out respectively for the fluoride, the chloride, the bromide and the iodide as 281 cm^{-1} , 187 cm^{-1} , 152 cm^{-1} and 131 cm^{-1} . The progressive diminution of the frequency is to some extent a consequence of the increasing atomic weight of the halogen, but it is chiefly the result of the diminishing strength of the binding between the metal and halogen atoms in the series. Expressed as infra-red wavelengths in microns, the corresponding figures are $35.6\ \mu$, $53.5\ \mu$, $65.8\ \mu$ and $76.3\ \mu$ respectively. These wavelengths agree with the positions in the spectrum of the maximum reflecting power for infra-red radiation reported in the literature for sodium fluoride and sodium chloride respectively, while no determinations of the rest-strahlen wavelength have been reported for the bromide or the iodide.

The vibration frequencies which we shall adopt for the calculation of the atomic heats for the four halides of sodium are listed below in table 1. There are certain differences between these figures and the frequencies computed and listed in part VI of the memoir. The justification for these changes will be stated later. The details of the computation of the atomic heat are exhibited in tables 2, 3, 4 and 5. The results are graphically exhibited in figures 1, 2, 3, and 4 below. No determinations of specific heat have been reported for sodium bromide in the temperature range between 0° and 300° K . Accordingly, figure 3 shows only the computed atomic heats. In figures 1, 2 and 4, the experimental values have been

Table 1. Atomic vibration frequencies (in cm^{-1})

	Degeneracies								
	3	4	8	4	8	6	3	3	6
NaF	285	270	260	246	236	240	210	187	144
NaCl	189	179	165	147	124	158	135	116	97
NaBr	163	144	144	77	77	152	144	76	60
NaI	140	129	129	55	55	133	129	54	43

shown alongside the computed curve to exhibit the agreement between theory and observation. It will be seen that this is quite satisfactory and particularly so in the case of sodium iodide where recent and reliable measurements of the specific heats are available.

Amongst the sodium salts, the fluoride stands in a class by itself. Its melting point is the highest, its refractive index the lowest and, excepting lithium fluoride, its aqueous solubility is the lowest and the bulk-modulus and the shear-modulus of elasticity the highest amongst all the sixteen halides. These facts indicate that the structure of sodium fluoride is held together by powerful interatomic forces. Its vibration frequencies should therefore be much higher than those of the corresponding modes of the other halides of sodium. Table 1 shows this to be the case.

The atomic weights of sodium and fluorine being not very different, the octahedral layers containing the one or the other species of atom alone have

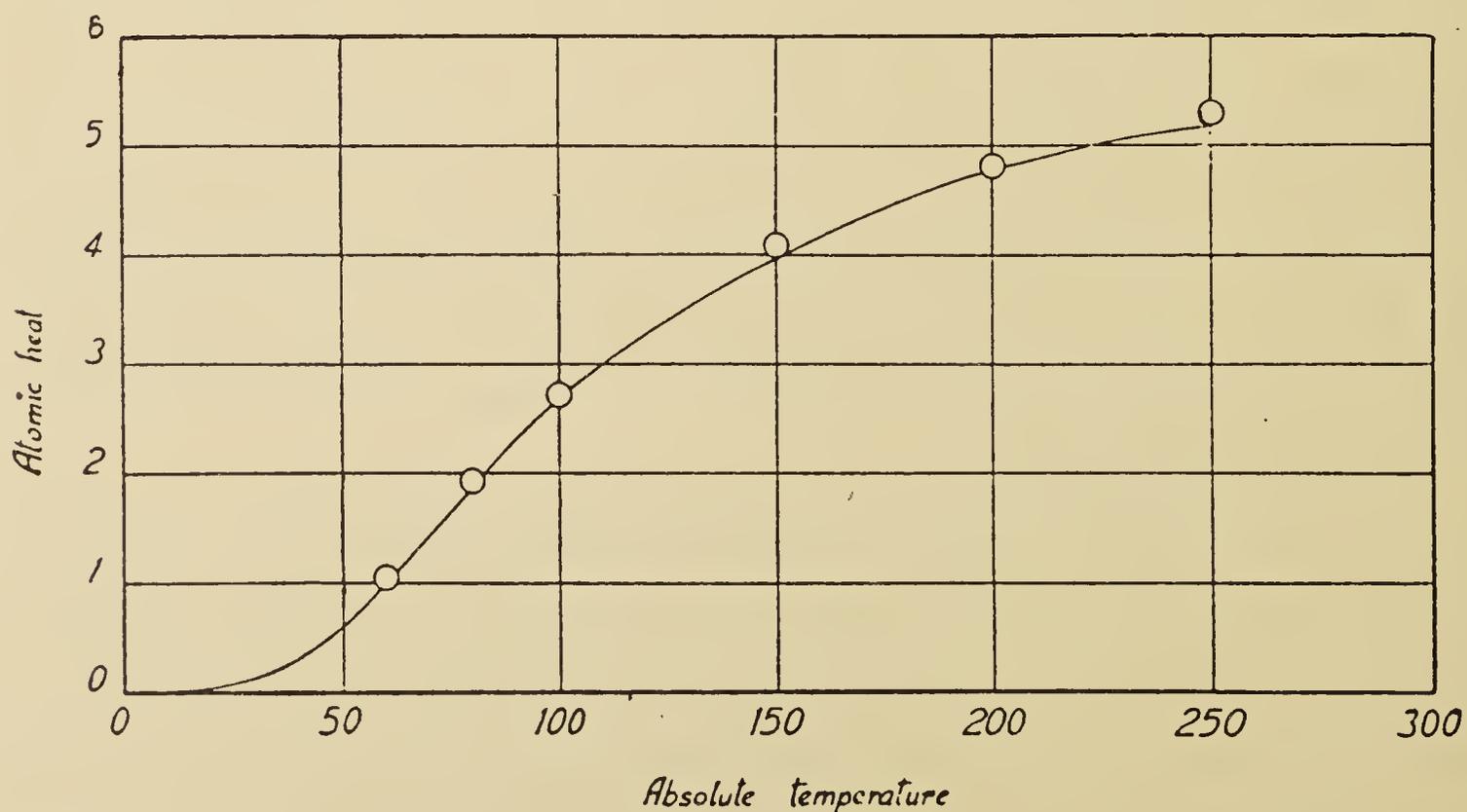


Figure 1. Atomic heats of sodium fluoride. C_v Computed values ————. C_p Observed values ○ ○ ○ ○.

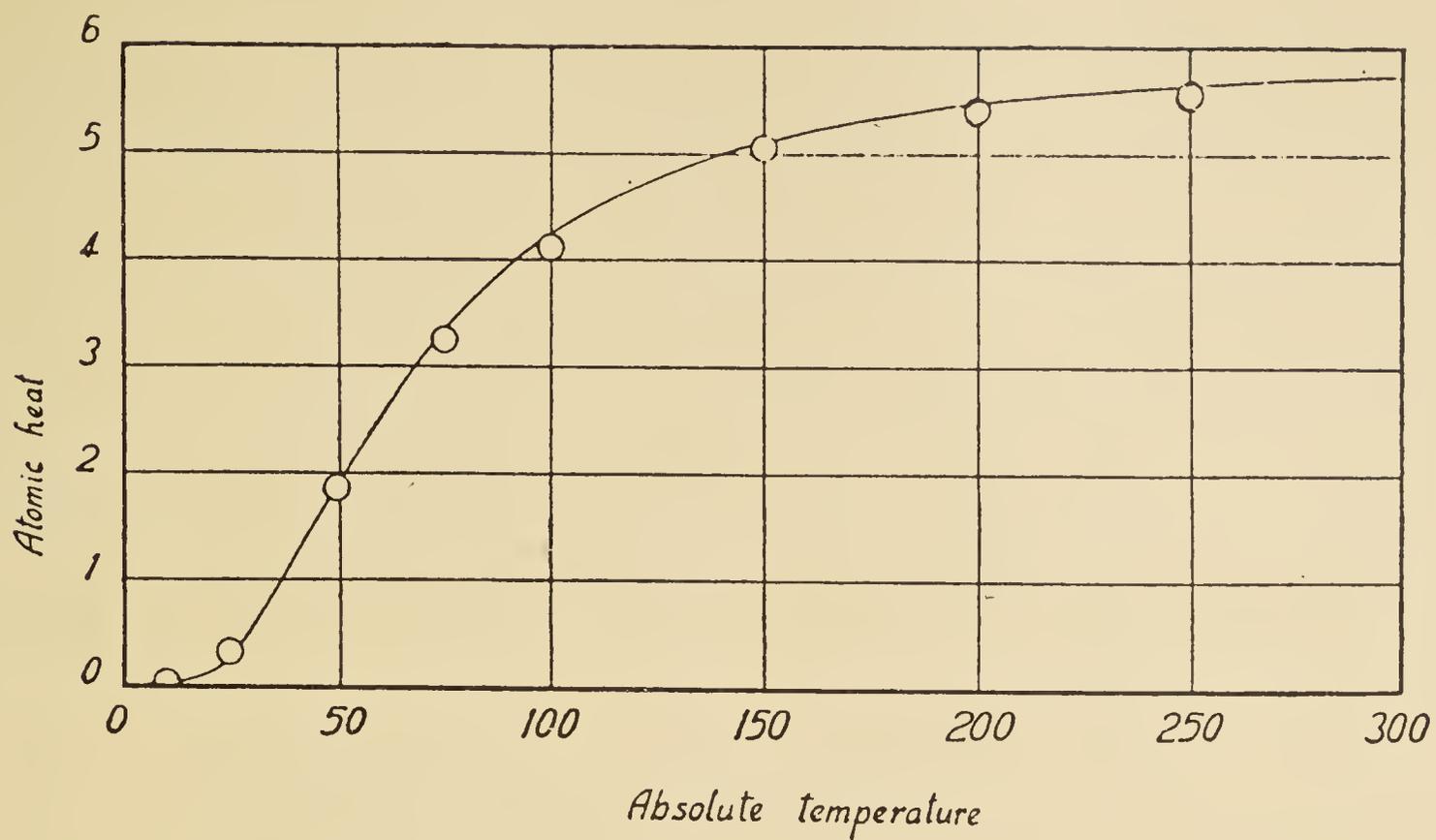


Figure 2. Atomic heats of sodium chloride. C_v Computed values ————. C_v Observed values ○ ○ ○ ○.

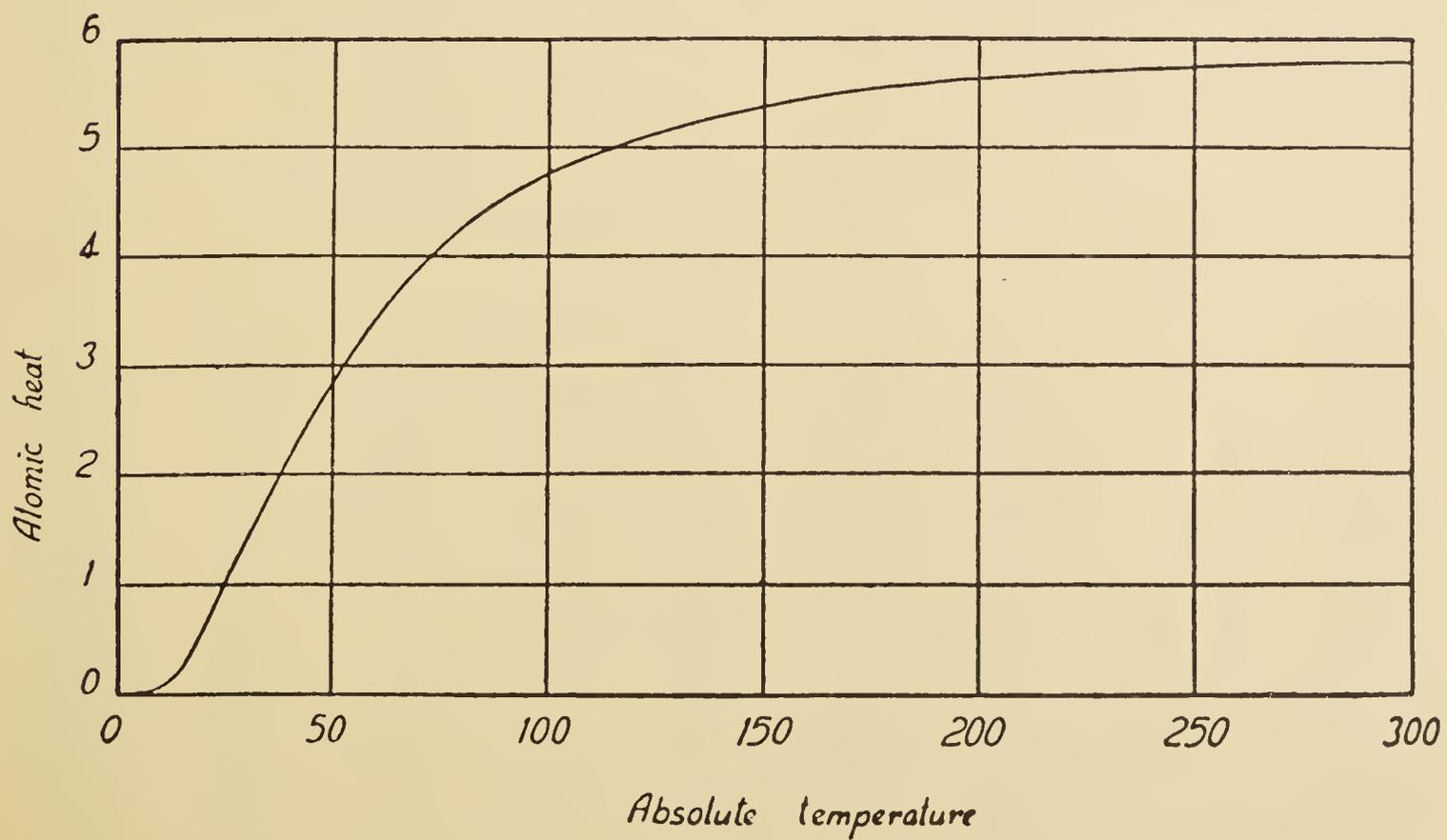


Figure 3. Atomic heats of sodium bromide (computed).

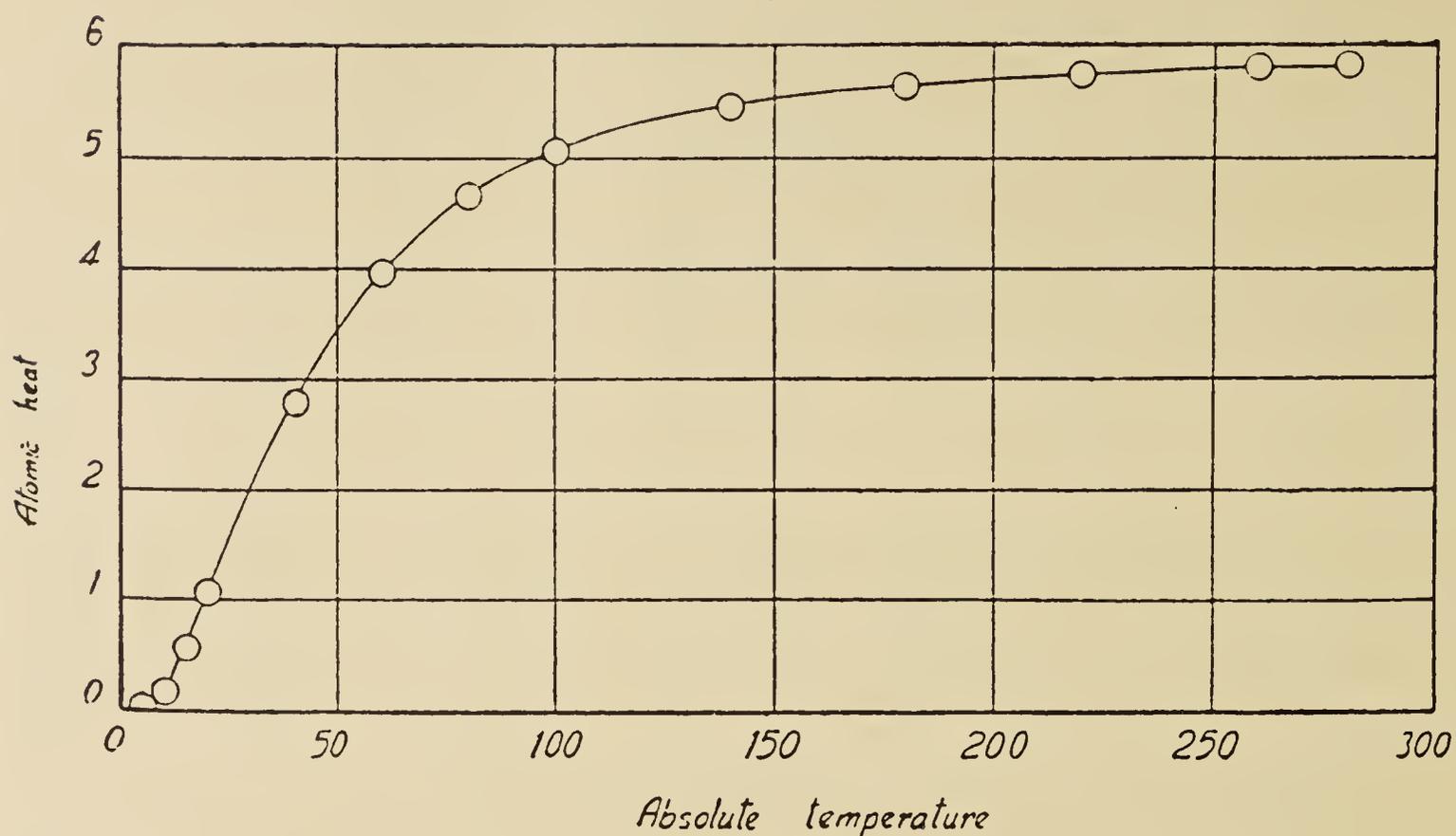


Figure 4. Atomic heats of sodium iodide. C_v Computed values ————. C_v Observed values ○ ○ ○ ○.

comparable frequencies of oscillation, those of the sodium atoms being a little lower. The position is reversed in respect of the other halides, where the halogens have much greater atomic weights. With the increasing mass of the halogen atoms, the oscillations of the layers containing them have progressively lower frequencies. This is shown by the entries on table 1. A somewhat similar situation also arises in respect of the two lowest frequencies of coupled oscillation of the atoms in the cubic layers.

Table 2. Computation of the atomic heats of sodium fluoride

	20° K	40° K	60° K	80° K	100° K	150° K	200° K	250° K
3E(285)	—	0.0012	0.0175	0.0561	0.1038	0.2037	0.2628	0.2974
4E(270)	—	0.0025	0.0301	0.0890	0.1560	0.2874	0.3629	0.4049
8E(260)	—	0.0068	0.0717	0.1983	0.3374	0.5977	0.7413	0.8219
4E(246)	—	0.0051	0.0452	0.1149	0.1868	0.3149	0.3827	0.4189
6E(240)	—	0.0090	0.0743	0.1836	0.2929	0.3578	0.5805	0.6341
8E(236)	—	0.0134	0.1059	0.2562	0.4021	0.6507	0.7804	0.8493
3E(210)	—	0.0103	0.0594	0.1239	0.1799	0.2662	0.3075	0.3283
3E(187)	0.0001	0.0189	0.0832	0.1530	0.2071	0.2846	0.3199	0.3382
6E(144)	0.0023	0.1088	0.2929	0.4312	0.5223	0.6341	0.6805	0.7023
3D(144)	0.0246	0.1266	0.2162	0.2697	0.3017	0.3383	0.3525	0.3594
Calc. C_v	0.0270	0.3026	0.9964	1.8759	2.6900	3.9354	4.7710	5.1547
Exptl. C_p *	—	—	1.065	1.929	2.714	4.089	4.804	5.307

*"Landolt-Bornstein" 6 Auflag, 4 Teil, II Bd., p. 486 (1961).

The forces which determine the atomic vibration frequencies in the alkali halides are *principally* those arising from relative displacements of the metal and halogen atoms attached to each other in the structure. It suffices to take them into account to obtain good approximation to the actual values of the atomic vibration frequencies. In particular, the highest vibration frequency is correctly given in the cases of LiF, NaF and NaCl where it is known from observational data. The same approximation also suffices as a basis for a computation of the atomic heats of the solids, and the results obtained are not unsatisfactory. But other interatomic forces of lesser magnitude have also to be considered if a complete quantitative agreement with the facts is to be obtained in all cases.

As has been pointed out in earlier parts of the memoir, the interactions between atoms of the same species do not appear in the equations of motion for the mode

Table 3. Computation of the atomic heats of sodium chloride

	10° K	25° K	50° K	75° K	100° K	150° K	200° K	250° K	300° K
3E(189)	—	0·0007	0·0463	0·1339	0·2029	0·2830	0·3185	0·3377	0·3471
4E(179)	—	0·0016	0·0739	0·1972	0·2897	0·3881	0·4312	0·4544	0·4662
8E(165)	—	0·0060	0·1902	0·4483	0·6252	0·8057	0·8802	0·9198	0·9417
6E(158)	—	0·0063	0·1606	0·3583	0·4863	0·6134	0·6678	0·6941	0·7089
4E(147)	—	0·0069	0·1288	0·2617	0·3436	0·4198	0·4523	0·4668	0·4761
3E(135)	—	0·0088	0·1170	0·2156	0·2721	0·3234	0·3439	0·3536	0·3591
8E(124)	—	0·0374	0·3680	0·6252	0·7611	0·8786	0·9283	0·9510	0·9637
3E(116)	—	0·0196	0·1552	0·2474	0·2950	0·3354	0·3506	0·3583	0·3627
6E(97)	0·0001	0·0837	0·3974	0·5577	0·6312	0·6920	0·7141	0·7247	0·7311
3D(97)	0·0102	0·1107	0·2573	0·3135	0·3373	0·3563	0·3630	0·3663	0·3682
Calc. C_v	0·0103	0·2817	1·8947	3·3588	4·2444	5·0957	5·4499	5·6267	5·7248
Exptl. C_v *	0·0170	0·3253	1·8620	3·2536	4·1244	5·0490	5·4040	5·5454	—

*Clusius K, Goldmann J and Perlick A *Z. Naturforsch.*, A4 424 (1949).

Table 4. Computation of the atomic heats of sodium bromide

	10° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K	250° K	300° K
3E(163)	—	0·0004	0·0346	0·1157	0·1872	0·2371	0·3029	0·3308	0·3455	0·3536
6E(152)	—	0·0014	0·0907	0·2650	0·4074	0·5017	0·6224	0·6739	0·6973	0·7115
3E(144)	—	0·0011	0·0544	0·1464	0·2156	0·2611	0·3171	0·3403	0·3511	0·3575
12E(144)	—	0·0045	0·2176	0·5858	0·8623	1·0445	1·2683	1·3610	1·4045	1·4300
12E(77)	0·0025	0·1718	0·8015	1·1219	1·2683	1·3447	1·4213	1·4508	1·4644	1·4732
3E(76)	0·0007	0·0453	0·2037	0·2821	0·3178	0·3369	0·3518	0·3630	0·3664	0·3683
6E(60)	0·0090	0·1836	0·5068	0·6254	0·6764	0·6983	0·7241	0·7328	0·7377	0·7406
3D(60)	0·0408	0·1669	0·2966	0·3354	0·3511	0·3582	0·3661	0·3687	0·3700	0·3707
Calc. C_v	0·0530	0·5750	2·2059	3·4777	4·2861	4·7825	5·3780	5·6213	5·7369	5·8054

Table 5. Computation of the atomic heats of sodium iodide

	5° K	10° K	15° K	20° K	40° K	60° K	80° K	100° K	140° K	180° K	220° K	260° K
3E(140)	—	—	0·0001	0·0014	0·0594	0·1537	0·2224	0·2662	0·3127	0·3354	0·3465	0·3536
6E(133)	—	—	0·0003	0·0043	0·1393	0·3331	0·4655	0·5493	0·6355	0·6774	0·6983	0·7106
3E(129)	—	—	0·0002	0·0027	0·0757	0·1736	0·2397	0·2797	0·3213	0·3403	0·3501	0·3566
12E(129)	—	—	0·0008	0·0108	0·3028	0·6944	0·9586	1·1186	1·2852	1·3610	1·4005	1·4265
12E(55)	—	0·0316	0·2043	0·4506	1·0751	1·2852	1·3713	1·4125	1·4495	1·4644	1·4743	1·4797
3E(54)	—	0·0088	0·0544	0·1170	0·2721	0·3234	0·3439	0·3536	0·3627	0·3664	0·3686	0·3702
6E(43)	0·0004	0·0556	0·2053	0·3472	0·6088	0·6805	0·7080	0·7204	0·7322	0·7377	0·7406	0·7414
3D(43)	0·0146	0·0905	0·1775	0·2381	0·3302	0·3525	0·3612	0·3650	0·3685	0·3700	0·3707	0·3712
Calc. C_v	0·0150	0·1865	0·6429	1·1721	2·8634	3·9964	4·6706	5·0653	5·4676	5·6526	5·7496	5·8098
Exptl. C_v^*	0·0147	0·1676	0·560	1·060	2·800	3·965	4·650	5·045	5·455	5·645	5·740	5·800

*Berg W T and Morrison J A, *Proc. R. Soc. (London)* A242 467 (1957).

of vibration having the highest frequency. But they do appear in the expressions for the other modes. In particular, they have a sensible influence on the oscillation frequencies of the atoms appearing in the octahedral layers. The magnitude of the corrections thus arising is known for the particular case of NaCl by reason of the availability of spectroscopic data for all its frequencies. Indeed, the figures for NaCl shown in table 1 are based on the observational studies and not those given by the approximate theoretical formulae.

The density of sodium fluoride is 2.79 and its lattice spacing 4.62 Å, as against 2.17 and 5.63 Å respectively for sodium chloride. There is thus good reason for assuming that the forces of interaction between atoms of the same species in sodium fluoride would influence the oscillation frequencies proportionately to an even greater extent than in the case for sodium chloride. These considerations determine the vibration frequencies of the octahedral layers computed and shown in table 1 for sodium fluoride. These are substantially higher than those calculated from the elastic constants and listed in part VII of this memoir.

The physical properties of sodium bromide and sodium iodide put them in a category different from the two other halides discussed above. Accordingly, their atomic vibration frequencies computed from the elastic constants have been taken over without substantial modifications and entered in table 1 above. Corrections have, however, been made to take account of the changes of the atomic vibration frequencies to be expected at the low temperatures covered by the specific heat determinations.

Summary

Computations of the atomic heats of the four sodium halides are presented and compared with the measured values. The spectroscopic data are the basis of the calculations in the case of NaCl and the atomic vibration frequencies determined from the elastic constants in the others. The vibration frequencies for NaF have been corrected to take account of the interactions between atoms of the same species which are strong in that crystal.

The specific heats of the alkali halides and their spectroscopic behaviour—Part XII. The potassium and rubidium salts

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Table 1 below reproduces the atomic vibration frequencies of the halides of potassium and rubidium calculated by the approximate method set out in part V of the memoir. Only two force-constants α and β appear in the formulae; α is a measure of the resistance to a change of bond-lengths and β to a change of the bond-angles in the crystal structure. The figures in table 1 are the same as those listed in part VI of the memoir but they are arranged in a slightly different manner. The highest frequency appears first, then the four frequencies of vibration of the octahedral layers and finally the frequencies of the four modes of coupled vibration of the atoms in the cubic layers. By reason of the neglect of all other atomic interactions except the two referred to above, the tangential and perpendicular modes of vibration of the octahedral layers appear in the table with identical frequencies. To this degree of approximation, they are both derivable from the highest frequency in a simple manner, being determined respectively by the masses of the two species of atoms in the structure as compared with the reduced mass which determines the highest frequency.

Table 1. The atomic vibration frequencies (cm^{-1})

	Degeneracies								
	3	4	8	4	8	6	3	3	6
KF	202	166	166	116	116	182	167	114	87
KCl	133	96	96	92	92	119	102	85	60
KBr	105	86	86	60	60	96	88	58	43
KI	90	79	79	44	44	84	80	42	32
RbF	167	151	151	71	71	158	152	69	55
RbCl	103	87	87	56	56	95	89	53	39
RbBr	78	56	56	54	54	71	63	47	33
RbI	64	49	49	40	40	59	53	36	26

As has been shown in part IV of the memoir, the two force-constants ϕ and ψ which express the interactions of the atoms of the same species with each other (metal and halogen respectively) do not appear in the formula for the highest frequency of vibration. Accordingly, we may expect the values for those frequencies shown in table 1 to correspond fairly closely with the observed behaviour of the respective crystals. Earlier in this memoir, it has been shown that this is the case for those halides of lithium and of sodium for which we have the necessary experimental data. We may therefore expect the same to be the case also for the halides of potassium and rubidium.

The infra-red wavelengths corresponding to the highest frequencies shown in table 1 are $50\ \mu$, $75\ \mu$, $95\ \mu$ and $111\ \mu$ respectively for the four halides of potassium and $60\ \mu$, $97\ \mu$, $128\ \mu$ and $156\ \mu$ for the four halides of rubidium. No studies appear to have been published on the infra-red behaviour of either potassium fluoride or rubidium fluoride. The reported results of the observations made with the six other halides on the reflections by their surfaces and on the absorption by thin films are not inconsistent with the figures given above. It should be remembered in this connection that studies of absorption and reflection in the region of such great wavelengths are beset with experimental difficulties and that the influence of the subsidiary modes has also to be taken into account in the interpretation of the observed effects.

In the preceding part of the memoir it was shown that the reported measurements of the atomic heats of sodium iodide from the absolute zero of temperature up to 270°K are faithfully represented by the theoretical computations based on the approximate formulae for the atomic vibration frequencies. Such a close agreement is presumably the result of the atomic weight of iodine being much greater than that of sodium. We may, therefore, reasonably expect that the thermal behaviour of lithium chloride, lithium bromide and lithium iodide and perhaps also of sodium bromide would likewise be faithfully represented by computations made on the same basis. Unfortunately, however, no experimental data on their specific heats have been reported for these same four halides.

The thermal behaviours of potassium fluoride and of potassium chloride may be expected to resemble those of sodium fluoride and sodium chloride respectively. In other words, it would be necessary to amend the approximate formulae for the vibration frequencies by taking into account the interactions between the atoms of the same species in their structures. Alternatively, it would be necessary to proceed on the basis of spectroscopic determinations of the atomic vibration frequencies. Potassium fluoride would be a difficult case to study by the available techniques. But the three other halides of potassium are distinctly more promising, since in their cases, the Rasetti technique for recording the doubled frequency shifts in light-scattering is available. Precise investigations of KCl, KBr and KI using that technique should enable a complete correspondence to be established between their thermal and spectroscopic behaviours.

Measurements of the specific heats of KCl, KBr and KI have been reported over a range of temperatures extending down to very low values. The measured values give the specific heats at constant pressure and need to be corrected to derive the specific heats at constant volume. These corrections are negligible at low temperatures but increase in importance with rising temperature. The values of the atomic heat thus corrected are exhibited in figure 1, the curves marked (1), (2) and (3) referring respectively to the iodide, bromide and chloride of potassium. The uncorrected values for potassium fluoride are shown in the curve marked (4). It will be seen that the values for potassium fluoride lie well below those of the other three halides and that the gaps between the curves (1), (2), (3) and (4) increase progressively, as is to be expected in view of the differences between the atomic vibration frequencies of the four halides shown in table 1.

As has already been remarked, we cannot expect the atomic heats of the potassium salts computed on the basis of the approximate frequencies listed in table 1 to fit the experimentally determined values in a perfect manner. Nevertheless, it appeared useful to make such computations and to present the results side by side with the atomic heats as measured and reported in the most recent investigations. Tables 2, 3, 4 and 5 exhibit the results respectively for the four potassium salts. It may be remarked that throughout the range of temperature covered by these tables, the computed atomic heats for the four halides follow each other in the same order as the observed values viz., $KI > KBr > KCl > KF$. When the computed values are represented graphically, they

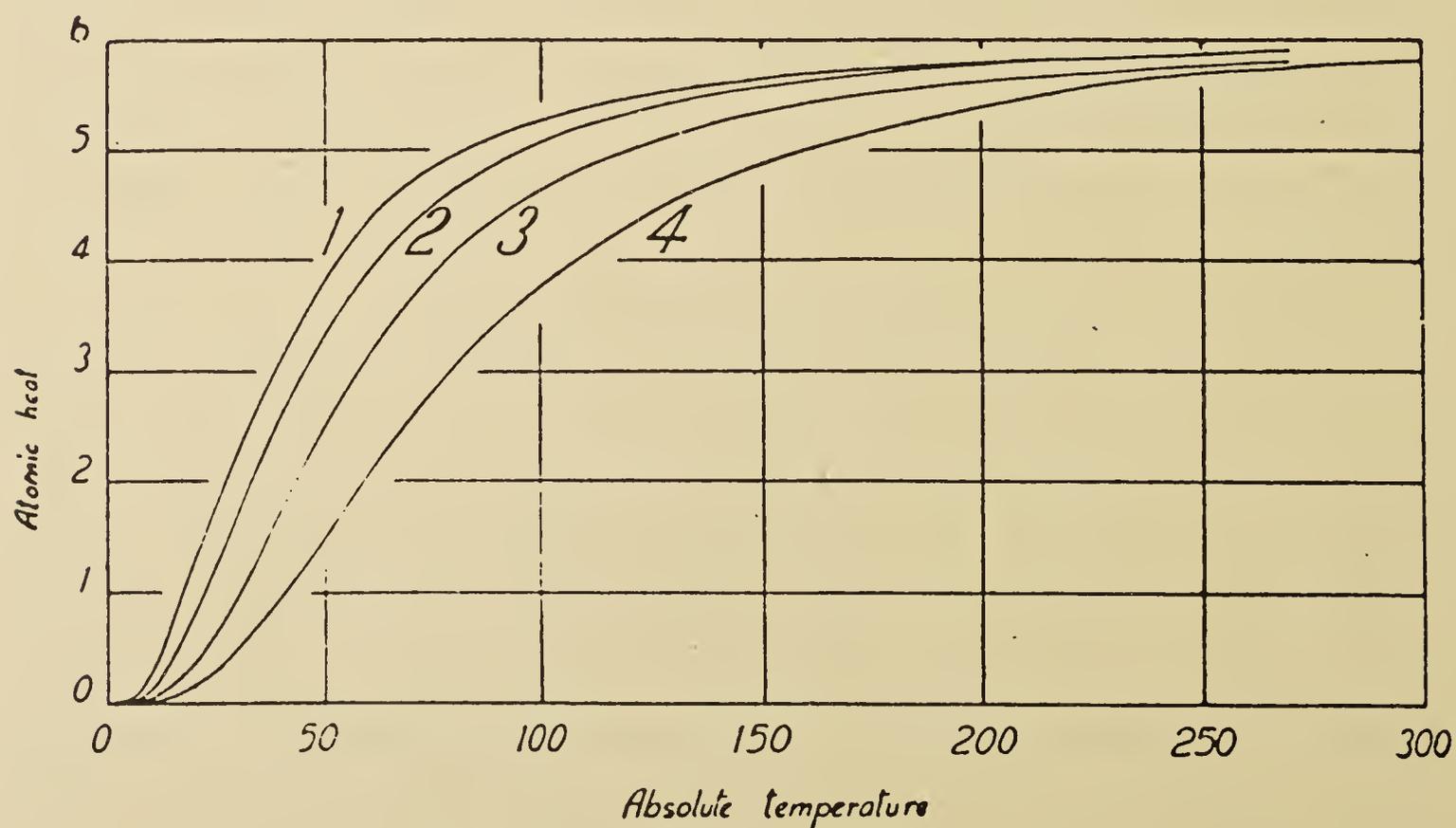


Figure 1. Experimental values of the atomic heats. (1) KI, (2) KBr, (3) KCl and (4) KF.

Table 2. Comparison of the computed and observed values of the atomic heats of potassium fluoride

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K	250° K	300° K
Calculated C_p	0.0145	0.0591	0.172	1.299	2.620	3.724	4.255	5.094	5.442	5.621	5.721
Experimental C_p	—	0.0377	0.139	0.946	2.089	3.044	3.776	4.863	5.398	5.698	5.858

Experimental values of C_p from Westrum Jr., E F and Pitzer, K S, *J. Am. Chem. Soc.*, **71**, 1940 (1949) as "Landolt-Bornstein" 6 Auflage, II Band, 4 Teil., p. 486.

Table 3. Comparison of the computed and observed values of the atomic heats of potassium chloride

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K	250° K
Calculated C_p	0.0506	0.215	0.552	2.582	3.969	4.702	5.105	5.557	5.726	5.808
Experimental C_p	0.0402	0.151	0.357	1.779	3.157	4.079	4.657	5.355	5.619	5.761

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc., (Lond.)* **A242**, 471 (1957).

Table 4. Comparison of the computed and observed values of the atomic heats of potassium bromide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
Calculated C_p	0.171	0.611	1.233	3.491	4.611	5.139	5.408	5.703	5.813
Experimental C_p	0.116	0.390	0.802	2.650	3.934	4.663	5.076	5.572	5.771

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc., (Lond.)* **A242**, 471 (1957).

Table 5. Comparison of the computed and observed values of the atomic heats of potassium iodide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
Calculated C_p	0.441	1.158	1.901	3.833	4.933	5.340	5.548	5.769	5.853
Experimental C_p	0.288	0.792	1.356	3.165	4.373	4.957	5.284	5.656	5.795

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc., (Lond.)* **A242**, 471 (1957).

appear as a family of non-intersecting curves similar to those for the experimental values shown in figure 1. They approach the axis of the abscissae at approximately the same temperatures and tend towards the maximum or limiting value in the same temperature range as the curves representing the experimental data. However, it is evident from tables 2, 3, 4 and 5 that the computed atomic heats are definitely larger than the observed ones. The percentage difference varies from halide to halide and also with the temperatures at which the two sets of values are compared.

The reason why the computed values are higher than the observed ones is not far to seek. Fully twenty-four out of every forty-eight degrees of dynamic freedom are manifested as the four modes of vibration of the atoms in the octahedral layers. These modes have, according to table 1, frequencies appearing in the middle range of the spectrum of each halide and hence they make the principal contribution to the atomic heat in the temperature range where it increases most rapidly. The neglect of the force-constants ϕ and ψ results in assigning to these modes frequencies which are distinctly less than the actual values. In consequence also, their computed contributions to the atomic heat are greatly exaggerated. It is not surprising that in these circumstances, the computed atomic heats exceed the observed values by large percentages.

By reason of the high atomic weights of both metal and halogen and the weakness of the binding between them, the vibration frequencies of rubidium bromide and rubidium iodide are quite low, as is seen from table 1. The position, however, is somewhat different in the cases of rubidium fluoride and rubidium chloride. These two halides are of special interest by reason of the great disparity between the atomic weights of the metal and the halogen which are their constituents. Unfortunately, however, no specific heat measurements are available for them.

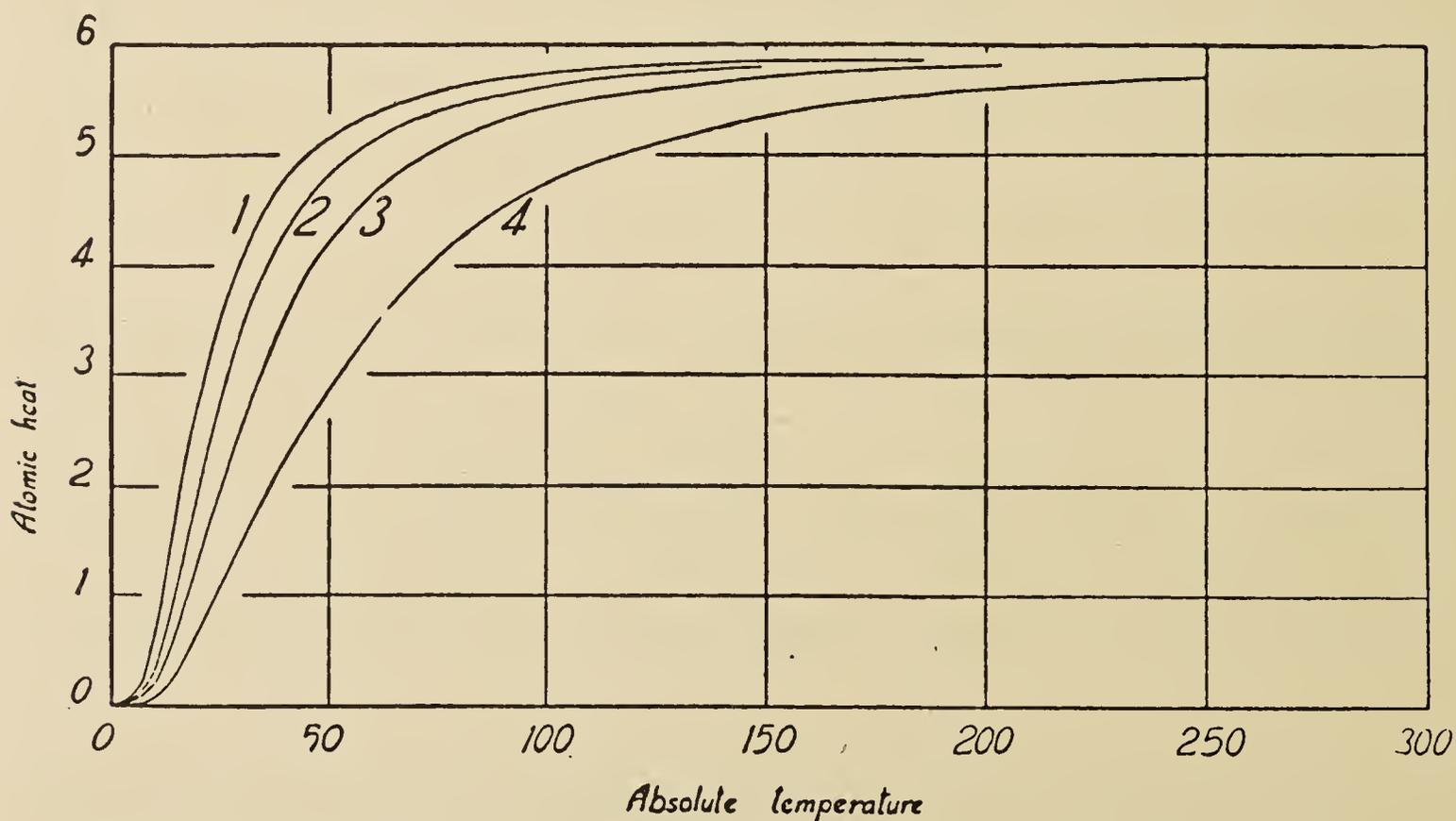


Figure 2. Computed values of the atomic heats. (1) RbI, (2) RbBr, (3) RbCl and (4) RbF.

The atomic heats of all the four rubidium salts have been computed on the basis of the frequencies listed in table 1 and are represented graphically in figure 2 above. The curves (1), (2), (3) and (4) marked in the figures refer respectively to RbI, RbBr, RbCl and RbF. The curves (3) and (4) are well separated from each

other and so also curves (2) and (3), though less conspicuously, while (1) and (2) fall close to each other. For reasons already explained, we cannot hope to find that the atomic heats thus computed for RbBr and RbI give a good fit with the experimental data available for these two halides. The comparison between the computed and observed atomic heats presented in tables 6 and 7 for the two cases indeed exhibits notable differences. The atomic heat falls so steeply in a narrow range of temperature in these cases that such differences are only to be expected.

We may here make a few remarks of a general nature. For some of the alkali halides, measurements of the elastic constants made at low temperatures are available. It is evident that the bulk-modulus and shear-modulus as determined at such temperatures and not those found by room-temperature measurements would be the proper basis for a computation of the atomic vibration frequencies from which the specific heats at low temperatures could be evaluated. The corrections to the frequencies needed on this account vary from halide to halide. In all cases, however, they do not exceed a few per cent, and in some cases, e.g., lithium fluoride, they are negligible.

Table 6. Comparison of the computed and experimental values of the atomic heats of rubidium bromide

	10.5° K	15.4° K	22.2° K	30.3° K	42.8° K	60.5° K	81.5° K	105.3° K	148.4° K
Calculated C_v	0.44	1.21	2.41	3.51	4.50	5.16	5.49	5.67	5.812
Experimental C_v	0.32	0.73	1.52	2.57	3.80	4.73	5.25	5.47	5.87

Table 7. Comparison of the computed and experimental values of the atomic heats of rubidium iodide

	12° K	16.3° K	20.3° K	27.3° K	39.8° K	68.6° K	129° K	189.5° K
Calculated C_v	1.15	2.09	2.84	3.84	4.79	5.52	5.83	5.87
Experimental C_v	0.78	1.27	1.85	2.85	4.08	5.27	5.79	5.90

Experimental values of the atomic heats of RbBr and RbI from Clusius K, Goldmann, J and Perlick, A *Z. Naturforsch.*, **A4**, 424 (1949).

Table 8. Computed values of the atomic heats of rubidium fluoride

Temperature °K	10	15	20	40	60	80	100	150	200	250
Calculated C_v	0.074	0.316	0.705	2.285	3.474	4.254	4.752	5.358	5.610	5.730

Table 9. Computed values of the atomic heats of rubidium chloride

Temperature °K	10	15	20	40	60	80	100	150	200
Calculated C_v	0.231	0.738	1.379	3.585	4.658	5.164	5.427	5.712	5.820

Summary

The atomic heats of the potassium and rubidium halides are computed on the basis of the table of vibration frequencies given in part VI and compared with the observed values in the cases for which these are available. The differences noticed are explained as arising from the octahedral modes having been assigned frequencies lower than the actual ones in the calculation.

The infra-red behaviour of sodium fluoride

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Sodium fluoride has the distinction of possessing the lowest refractive index of any crystalline solid, being about the same as that of water which is 1.333. It has the same crystal structure as rock-salt. But its infra-red reflection maximum appears at a much smaller wavelength, viz., 36μ , than that of rock-salt which is at 54μ . Hence, the infra-red behaviour of NaF is more readily accessible to investigation than that of NaCl.

Synthetically prepared crystals of NaF of excellent optical quality are available. A rectangular block of NaF $40 \text{ mm} \times 21 \text{ mm} \times 21 \text{ mm}$ in size was procured from Dr Karl Korth of Kiel, West Germany. The material had a perfect cleavage parallel to the faces of the block, making it possible to obtain plates of various thicknesses for a detailed study of its infra-red absorption. The aim of the investigation was to establish the relationship between the absorption spectra of the material and the activities of the various modes of free vibration of the structure set out and discussed in a recently published memoir¹ by the present author.

In the memoir under reference, the principles of classical mechanics were employed to deduce the normal modes of free vibration of the atoms in crystals having the rock-salt structure. It emerged that the vibrational mode of highest frequency is that in which the atoms of metal and halogen oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described simply in terms of the crystal structure; four of the modes are oscillations of the cubic layers, while the other four modes are oscillations of the octahedral layers of the structure, the movement alternating in phase from layer to layer, and being either normal or tangential to those layers. Since the oscillations of the metal and halogen atoms may be either in the same phase or in opposite phases, we have four modes for the cubic layers and four modes for the octahedral layers and hence eight in all. The oscillations of the metal and halogen atoms in the cubic layers would be coupled with each other, since both sets of atoms appear interspersed in these layers. But the oscillations of the metal and halogen atoms in the octahedral planes would appear independently since they are located in distinct and alternating layers in these planes.

It was further shown in the memoir that approximate expressions for the frequencies of the free modes of vibration could be obtained in terms of *two* force-constants only. The first force-constant α expresses the resistance to a longitudinal movement of the neighbouring metal and halogen atoms in the structure with respect to each other. The second constant β is the force which expresses the resistance to a transverse relative displacement of these atoms. α and β were numerically evaluated from the relations $\alpha = k \times d$ and $\beta = c_{44} \times d$ where d is the spacing of the cubic layers, k is the bulk modulus and c_{44} is the shear-elasticity of the crystal. The frequencies thus calculated were tabulated in the memoir.

In table 1 below, the fundamental frequencies thus computed of the mode of highest frequency and of the four modes of coupled oscillation of atoms in the cubic layers for NaF have been shown converted into infra-red wavelengths to facilitate comparison with the observational data. The four modes of oscillation of the atoms in the octahedral layers have not shown, as they are totally inactive. Besides the wavelengths corresponding to the fundamental frequencies, the wavelengths corresponding to the overtones up to the fourth have also been listed.

Table 1. Wavelengths in microns

Modes	I	II	III	IV	V
Fundamentals	35.6	41.5	47.6	53.5	69.4
First overtones	17.8	20.8	23.8	26.7	34.7
Second overtones	11.9	13.8	15.8	17.8	23.1
Third overtones	8.9	10.4	11.9	13.8	17.4
Fourth overtones	7.1	8.3	9.5	10.7	13.5

The infra-red activity with which we are principally concerned is that of the principal mode of highest frequency, both as a fundamental and as its various overtones. Its fundamental wavelength lies outside the ranges covered by the NaCl and KBr optics of the recording spectrophotometer. Its first, second, third and fourth overtones, however, fall within the range of these instruments. Hence, it should be possible to find evidence of the absorptions due to them at or near the wavelengths (using round figures) 18μ , 12μ , 9μ and 7μ respectively. The strength of these absorptions would naturally diminish rapidly with their increasing order. Hence, greater and greater absorption paths would be needed to exhibit the absorptions of higher orders. We cannot altogether ignore the absorptions of the second and higher orders due to the four other modes of free vibration listed in table 1. The superposition of their effects on those due to the overtones of the fundamental of highest frequency would tend to smooth out the step-like character of the falls in absorption to be expected at the wavelengths 18μ , 12μ , 9μ and 7μ . These falls should nevertheless appear clearly enough to be recognized in the spectrophotometer records.

The foregoing remarks prepare the ground for an understanding of the features noticeable in the series of spectrophotometer records reproduced as figures 1 to 12 in the text. The largest absorption path is 21 mm and the smallest is 0.18 mm, one being more than a hundred times greater than the other. The very great differences in the magnitudes of the specific absorptions recorded with these thicknesses will thus be evident.

The most significant result revealed by the investigation is the sharply-defined peak of absorption at 18.2μ seen in figures 10, 11 and 12 which are the records obtained with the three thinnest plates of the series. These three figures show a large and steep fall in transmission in the range of wavelengths immediately preceding the minimum of transmission at 18.2μ . In figures 7, 8 and 9 recorded in the KBr range with plates of thicknesses 2 mm, 1 mm and 0.65 mm respectively, the transmission also falls in the same range of wavelengths but it ends in a cut-off at 18μ beyond which there is no transmission. These features make it clear that the wavelength 18μ represents the boundary between the regions in which the third and second-order absorptions due to the fundamental mode of highest frequency are respectively effective, and that the sharply-defined peak of absorption at 18.2μ gives us the precise frequency of the octave of that mode;

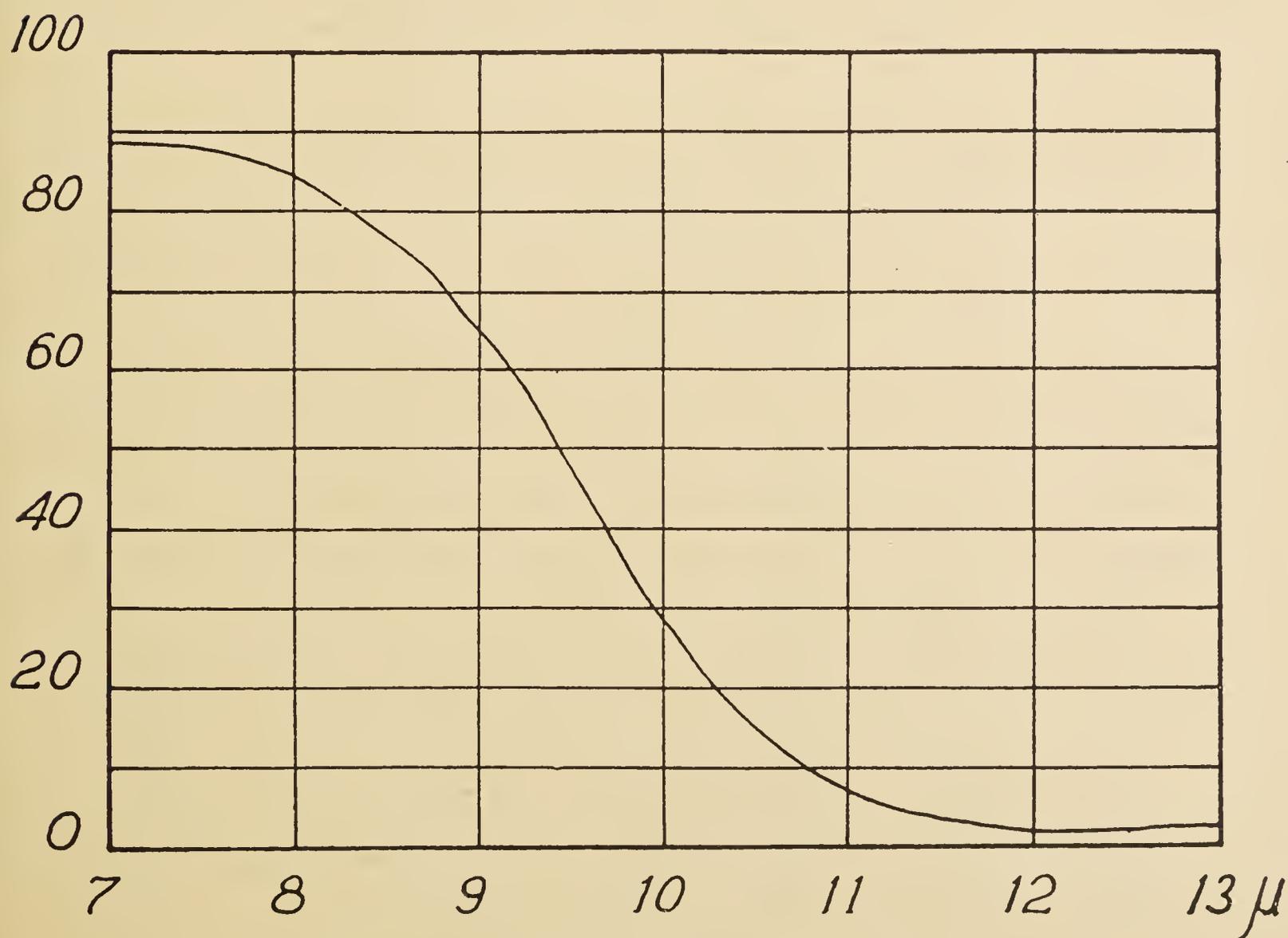


Figure 1. Absorption by NaF; plate thickness: 21 mm.

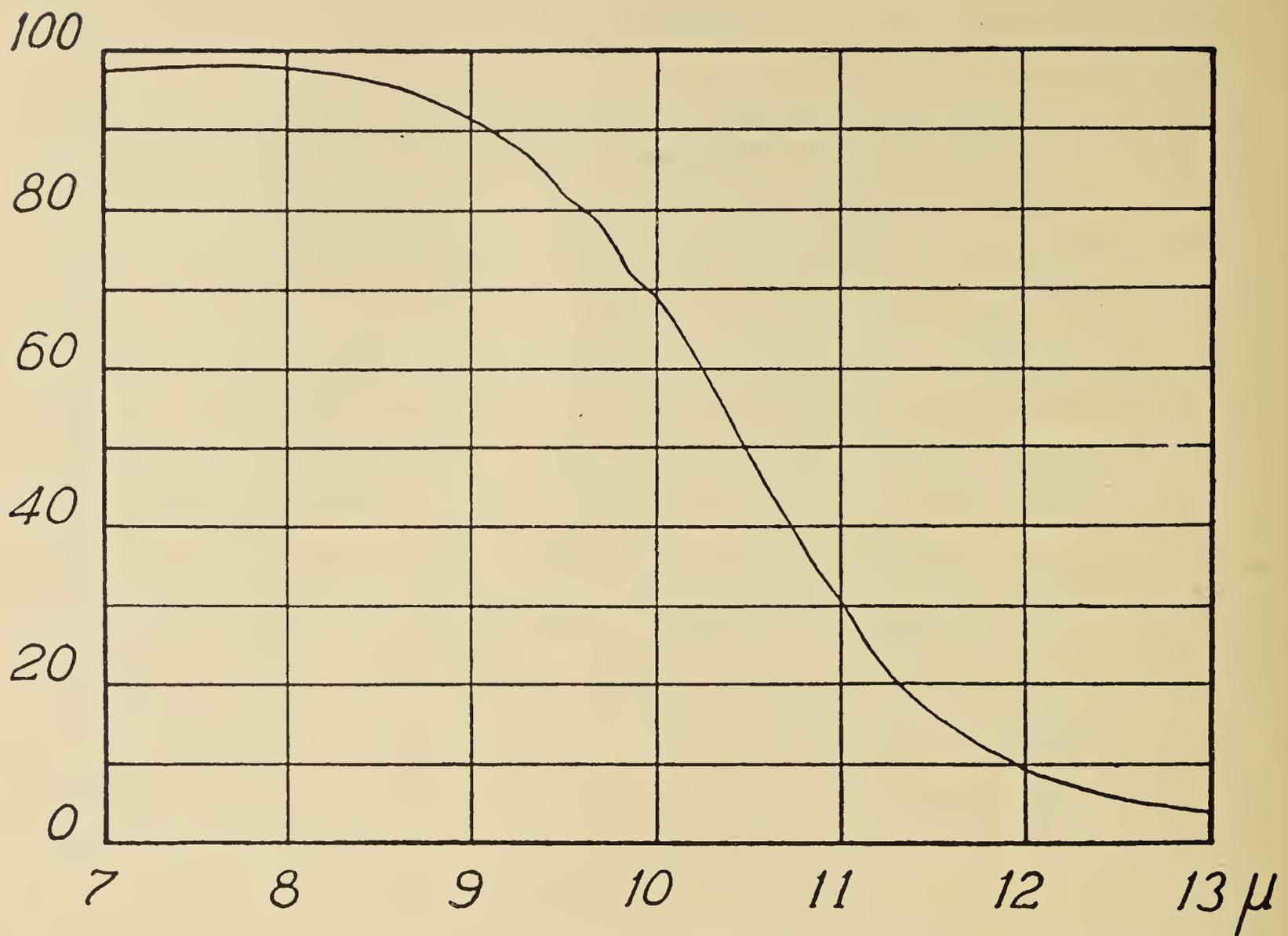


Figure 2. Absorption by NaF; plate thickness: 8 mm.

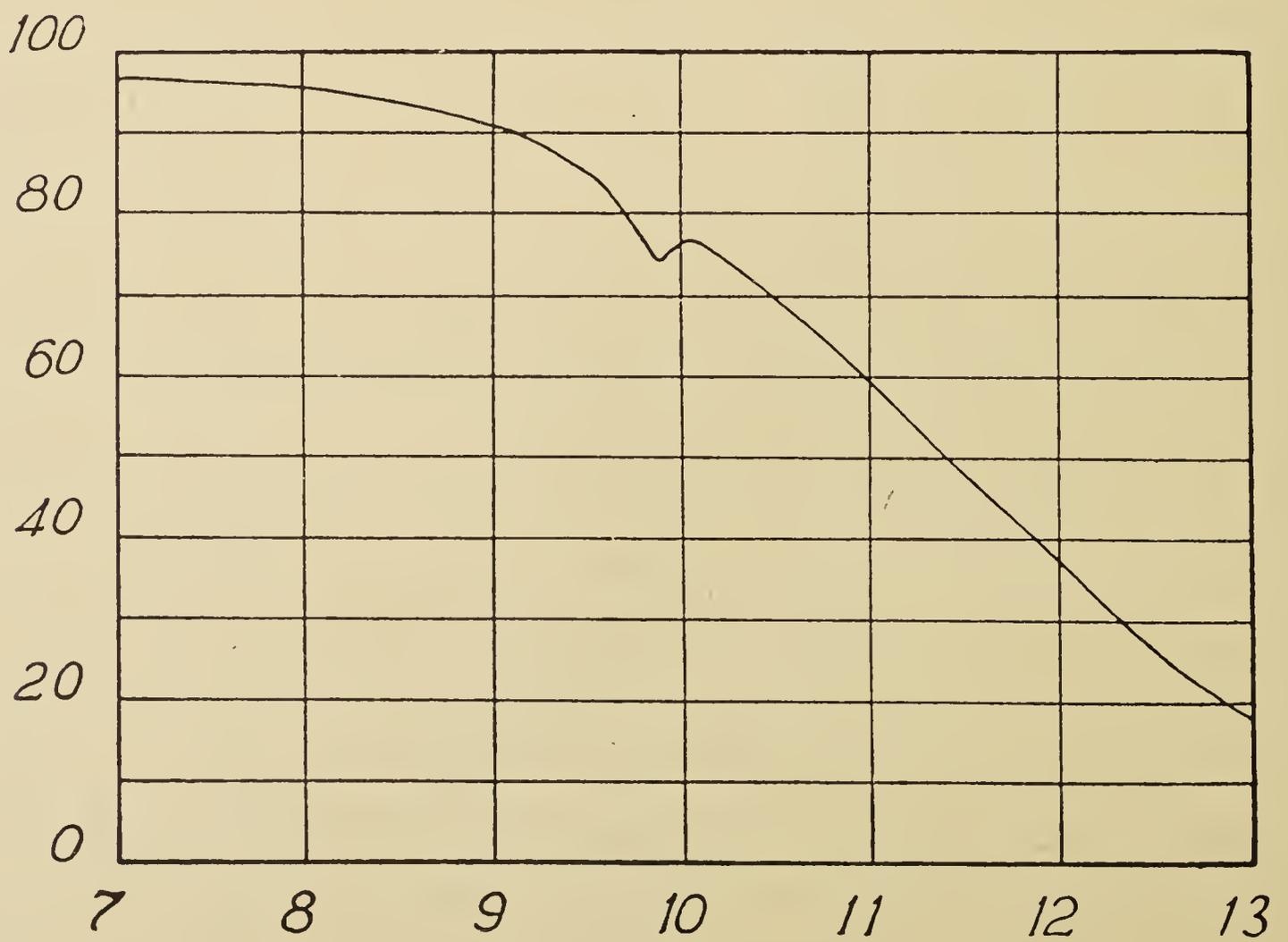


Figure 3. Absorption by NaF; plate thickness: 3 mm.

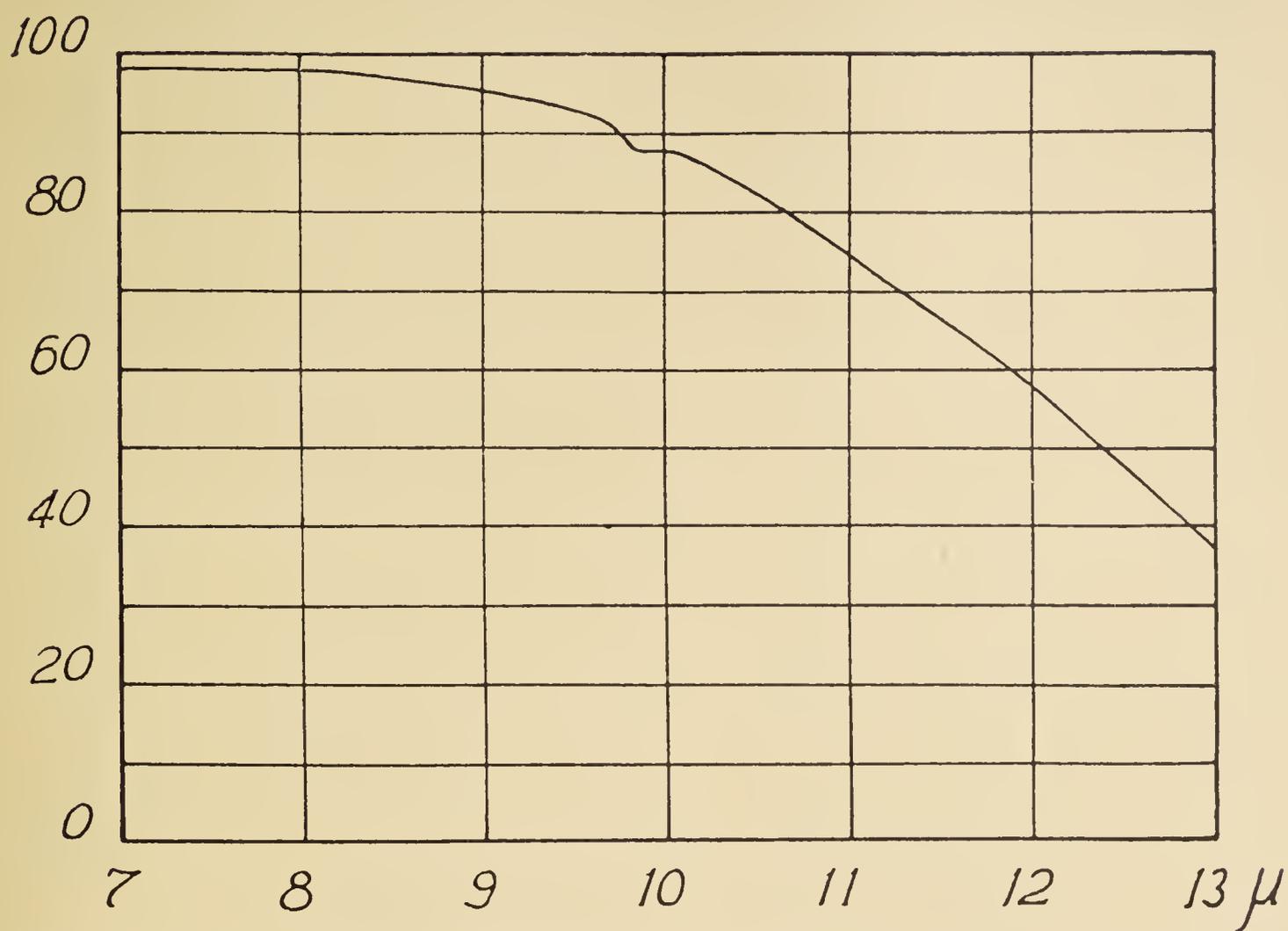


Figure 4. Absorption by NaF; plate thickness: 2 mm.

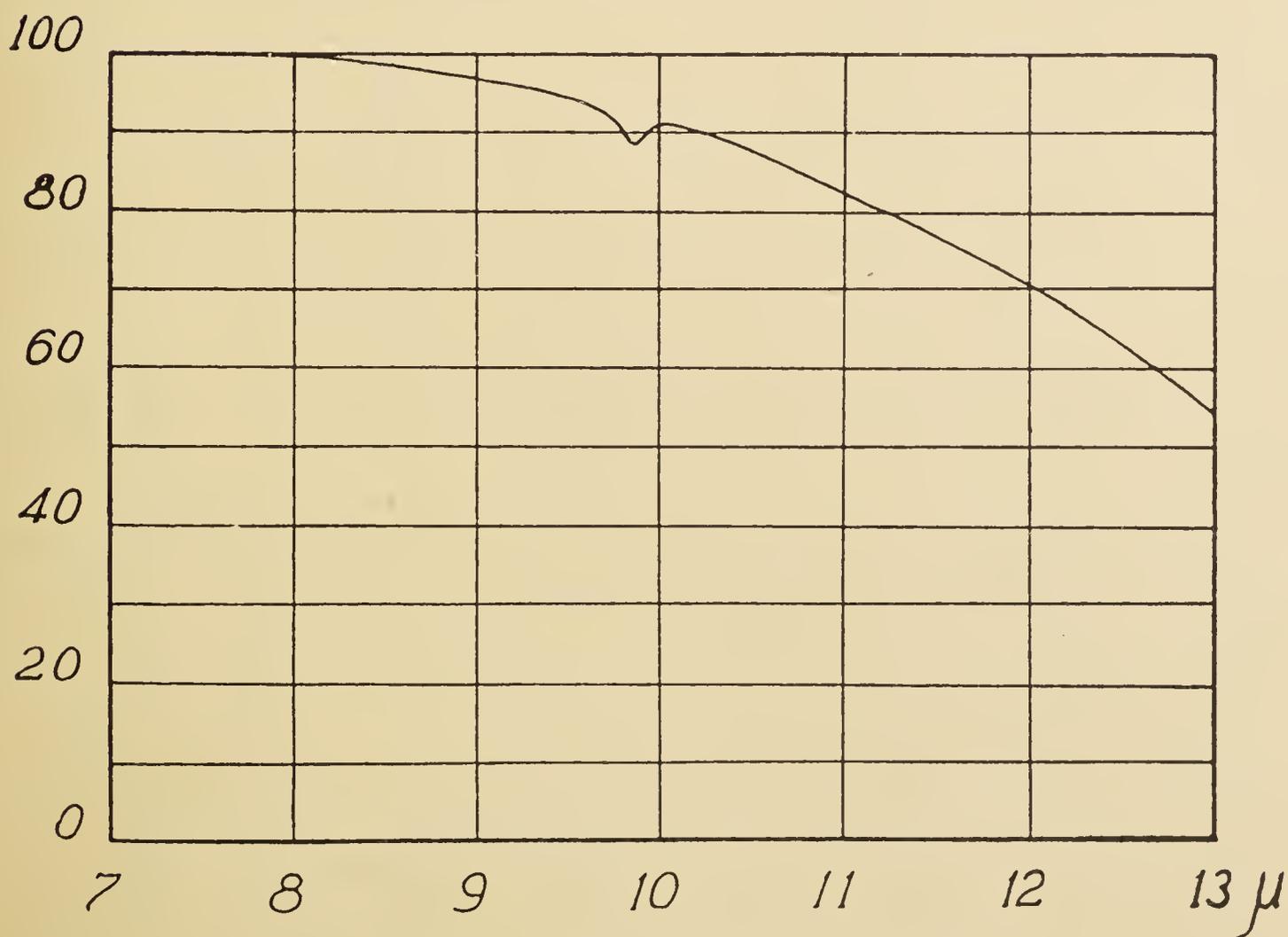


Figure 5. Absorption by NaF; plate thickness: 1 mm.

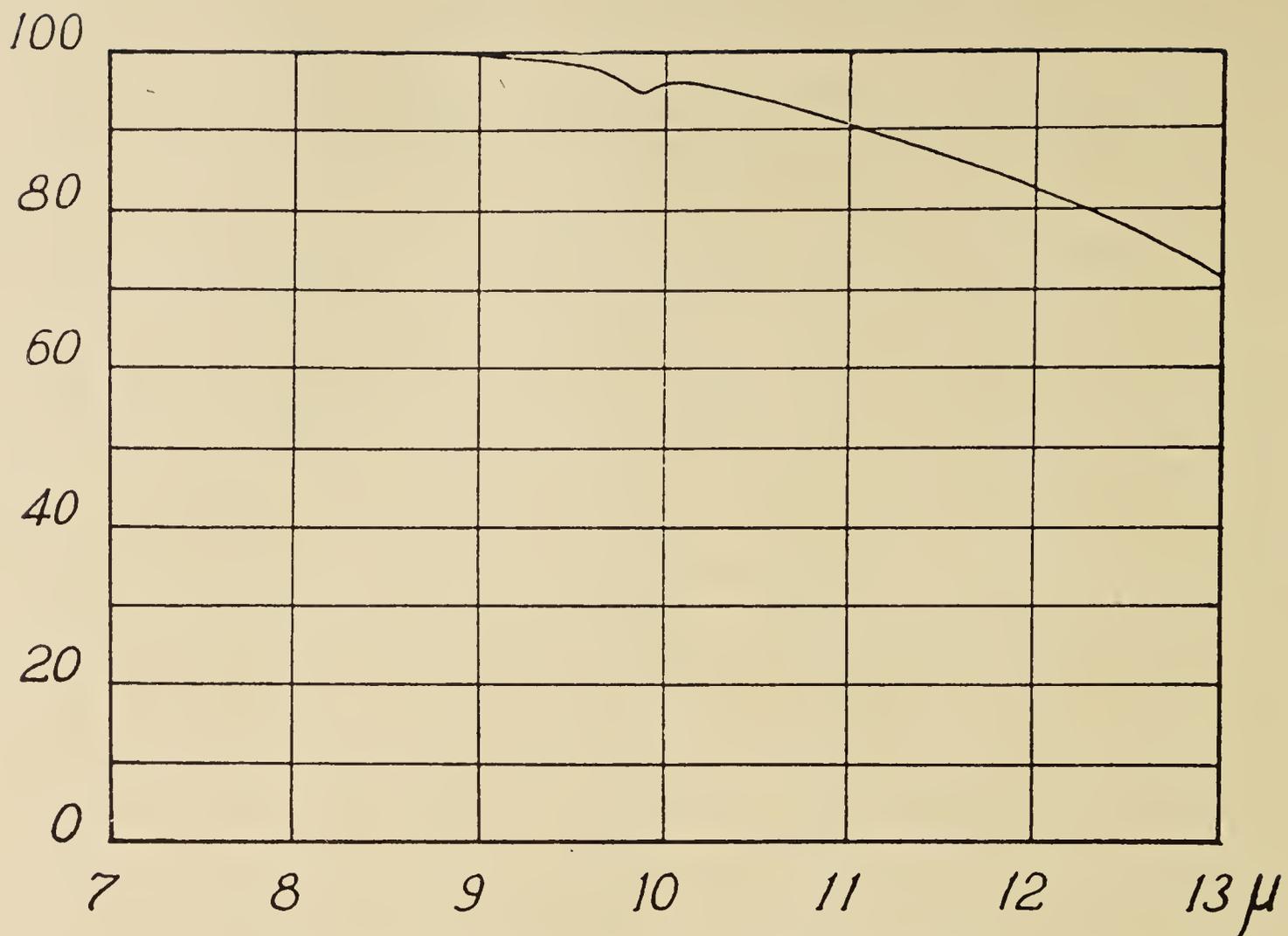


Figure 6. Absorption by NaF; plate thickness: 0.65 mm.

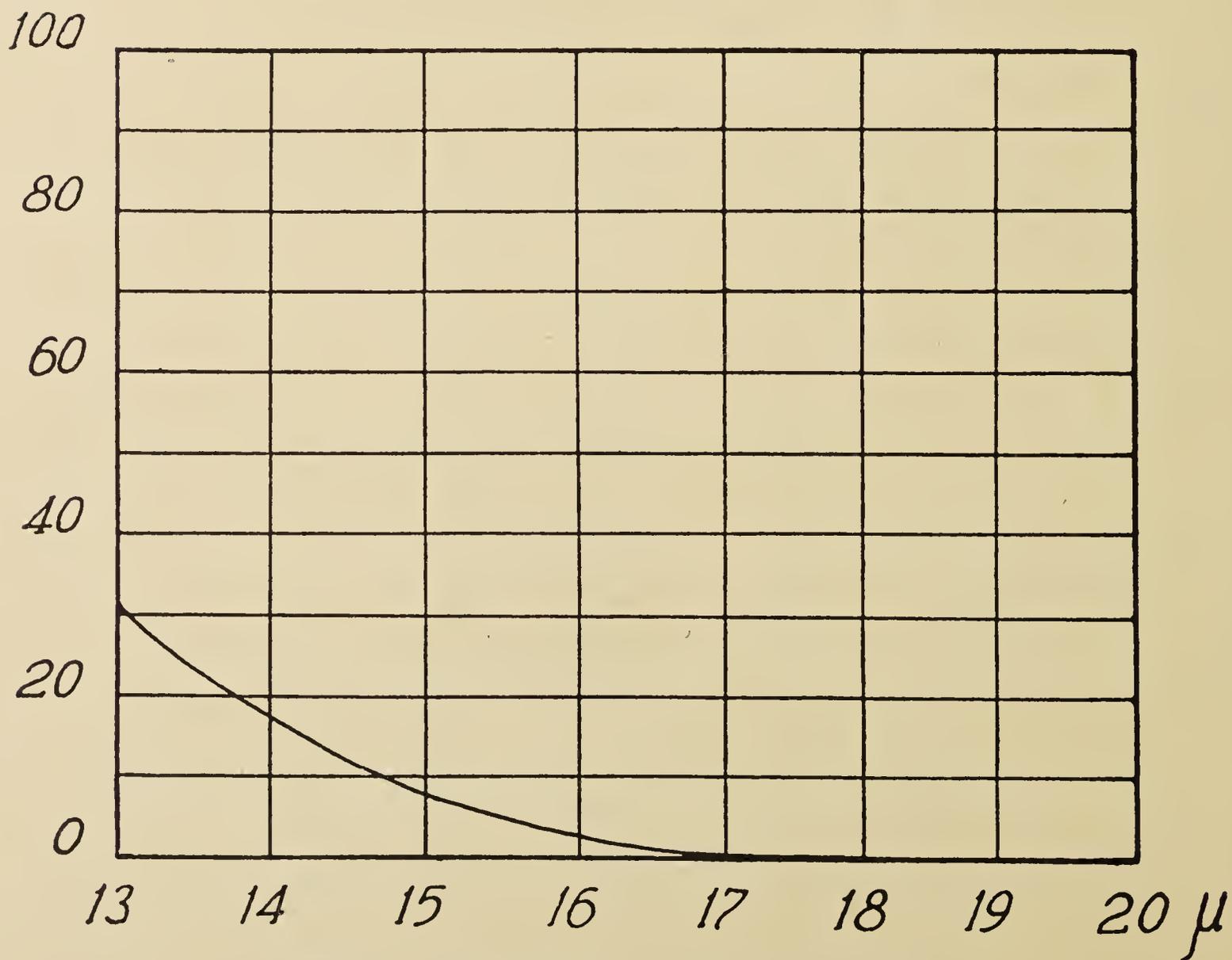


Figure 7. Absorption by NaF; plate thickness: 2 mm.

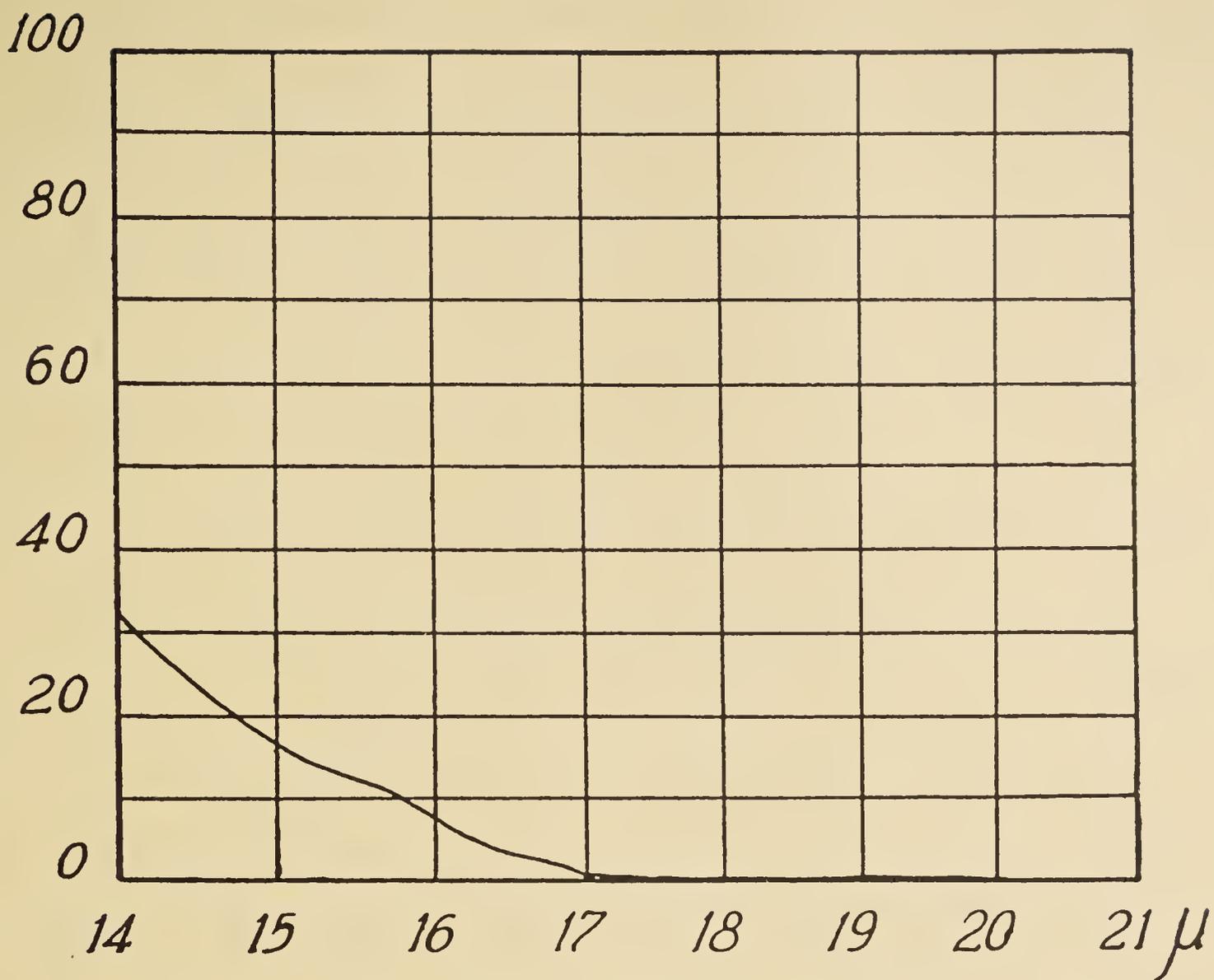


Figure 8. Absorption by NaF; plate thickness: 1 mm.

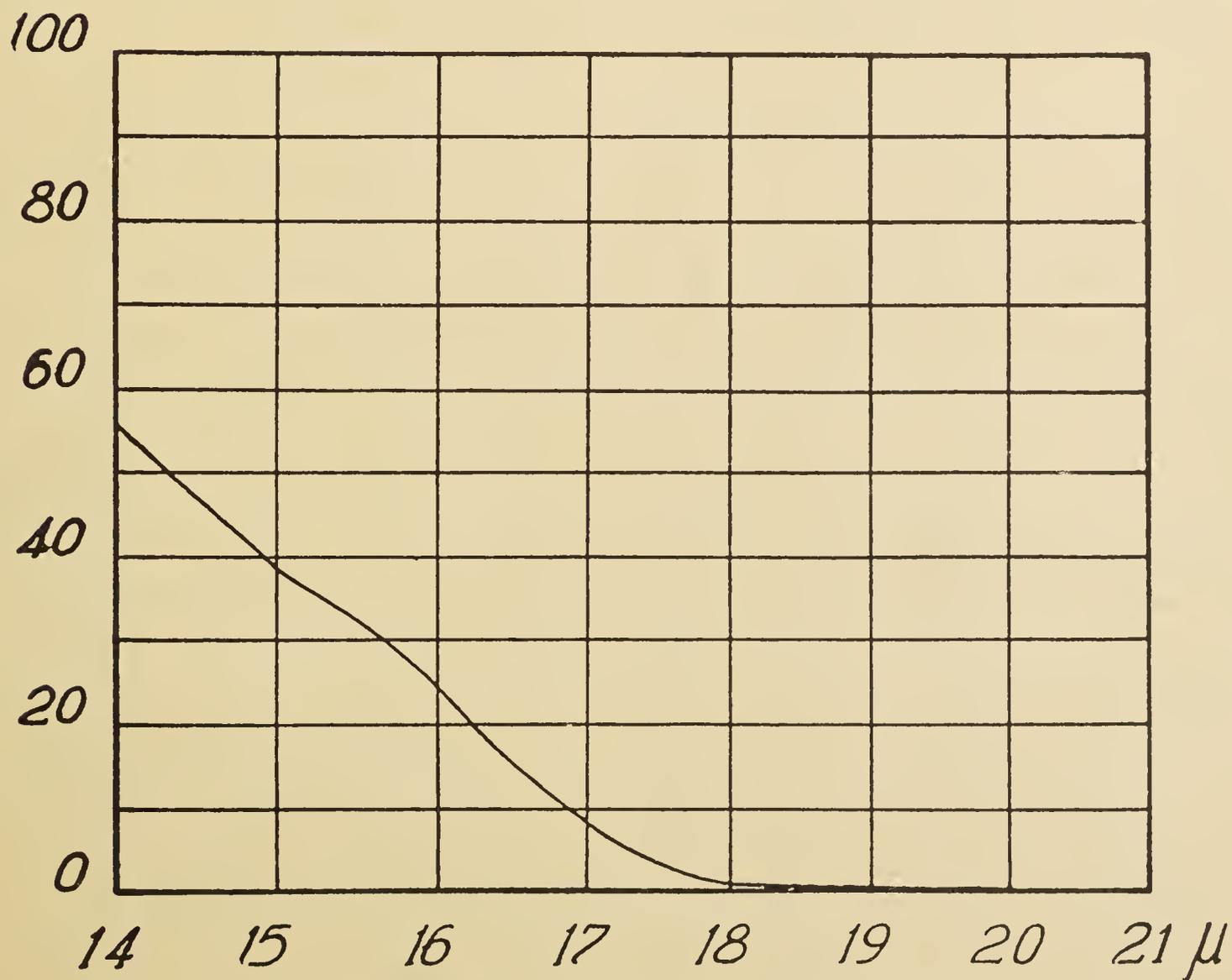


Figure 9. Absorption by NaF; plate thickness: 0.65 mm.

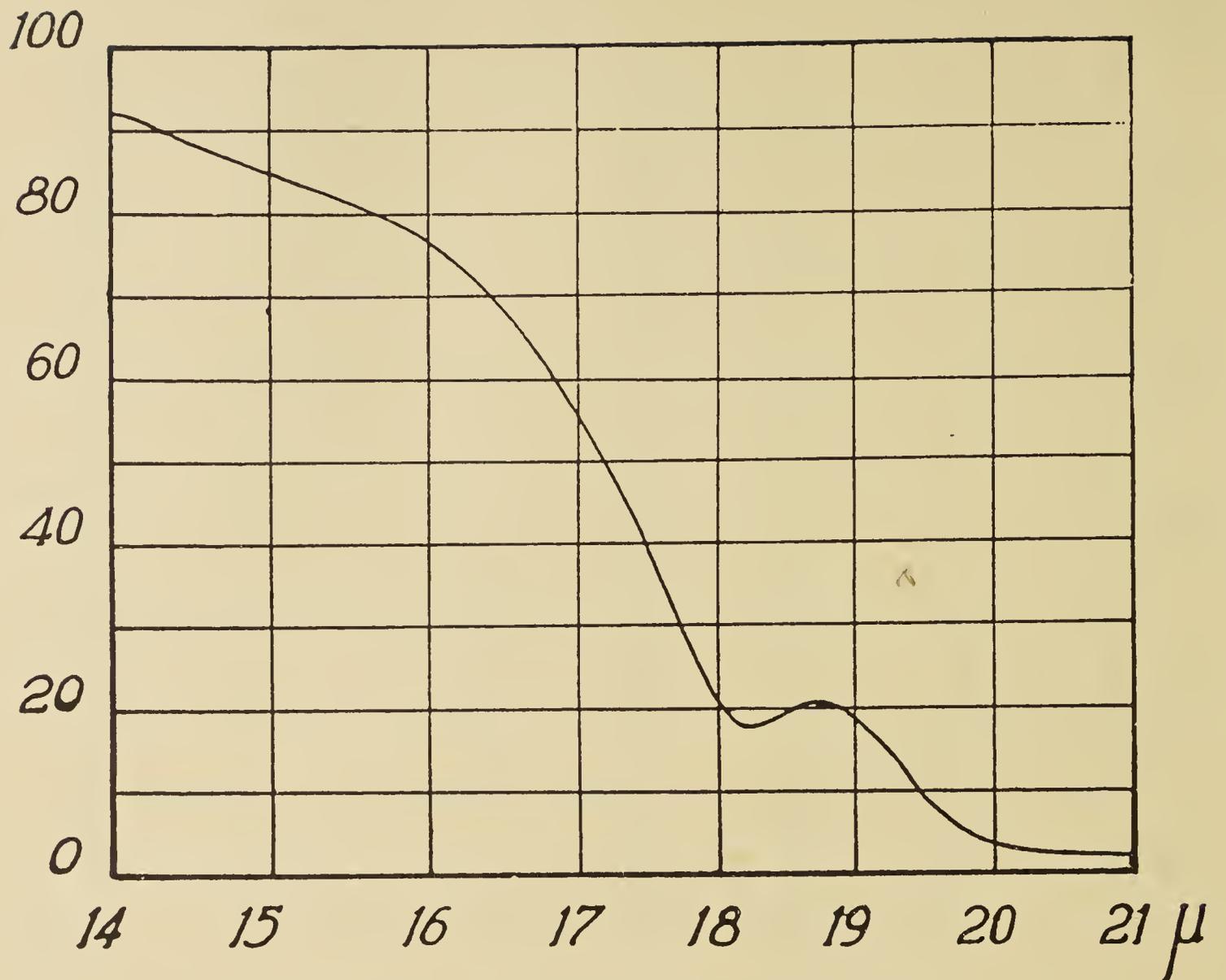


Figure 10. Absorption by NaF; plate thickness: 0.36 mm.

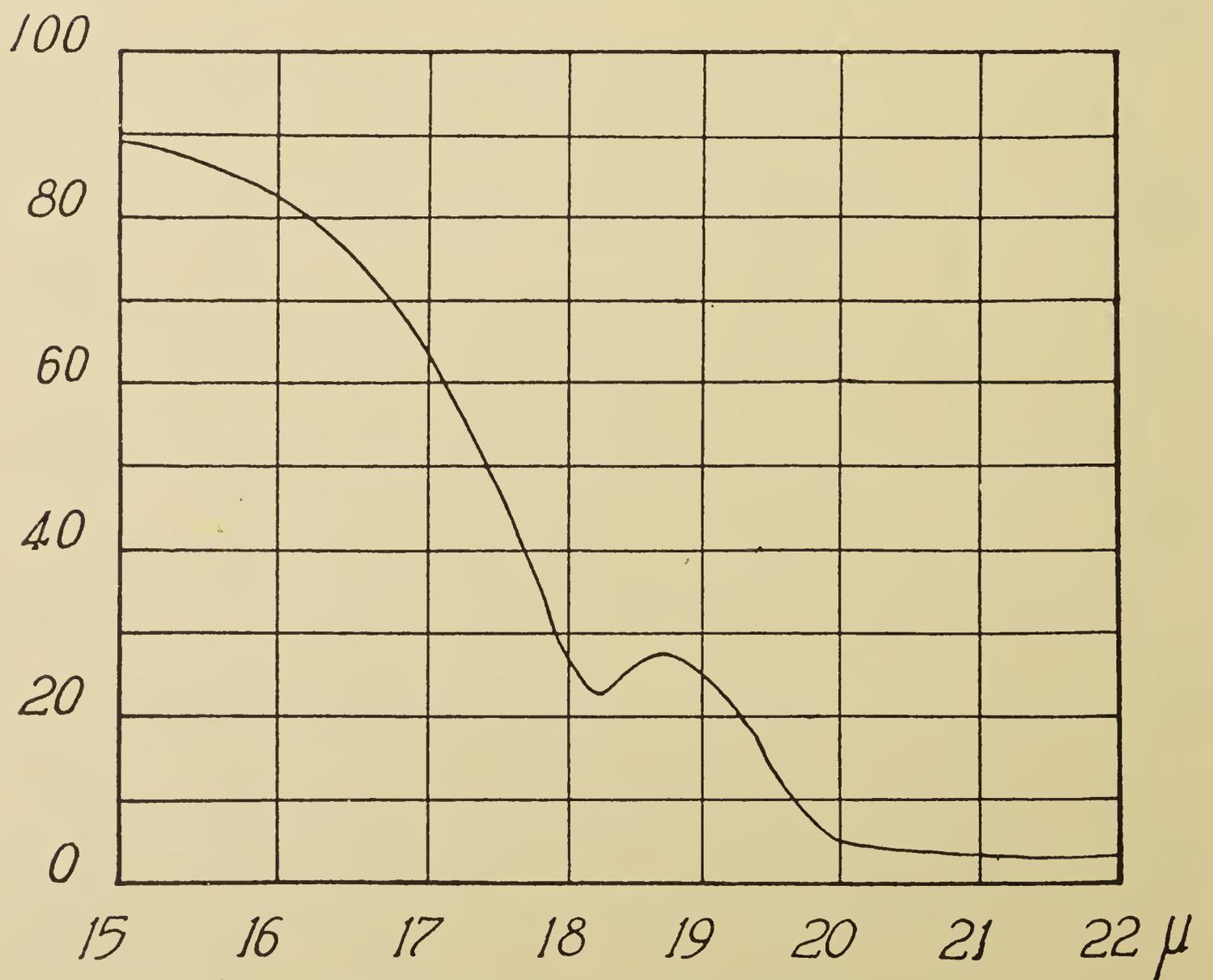


Figure 11. Absorption by NaF; plate thickness: 0.25 mm.

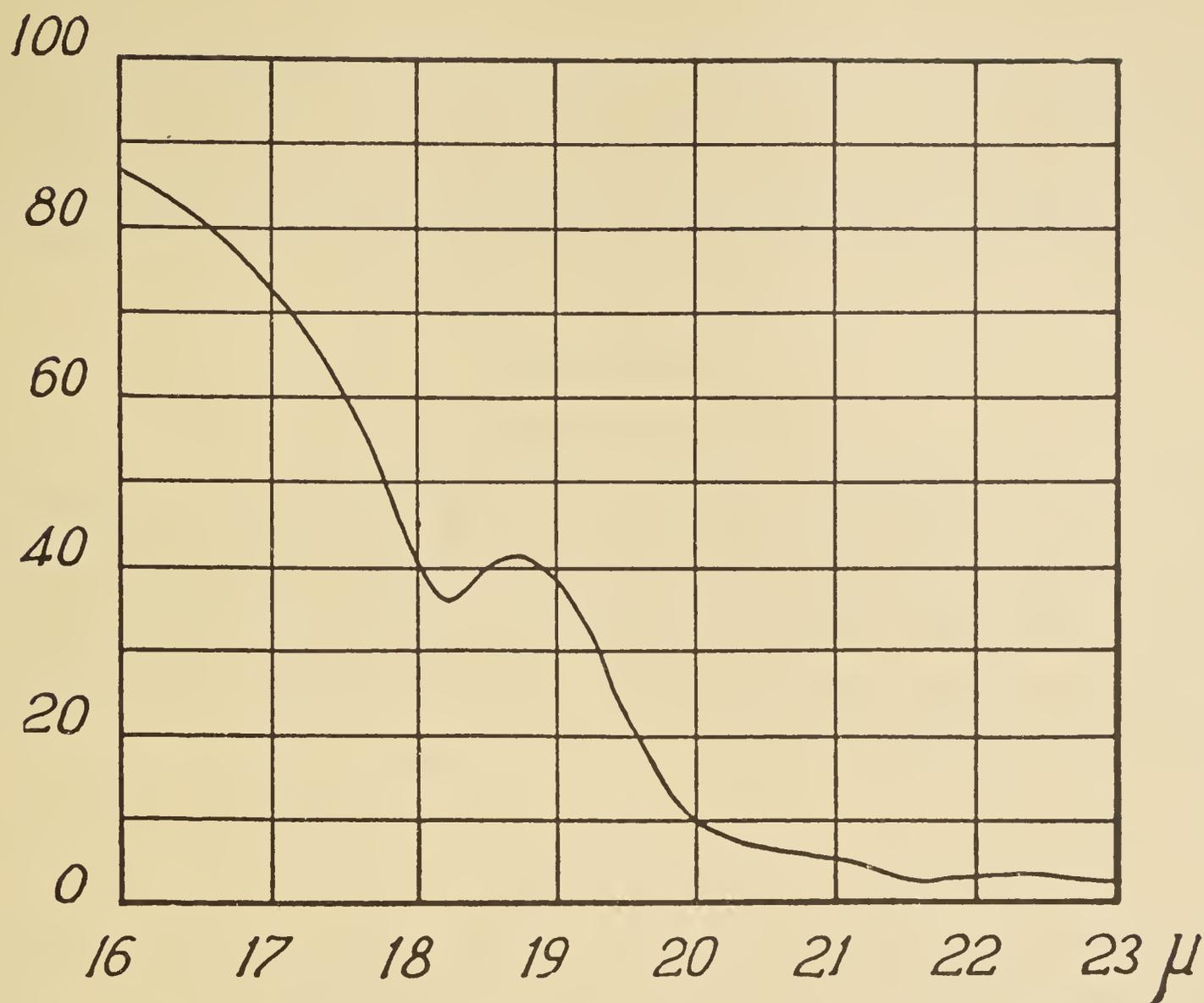


Figure 12. Absorption by NaF; plate thickness: 0.18 mm.

expressed as a wavelength, the fundamental is 36.4μ and as a wave-number it is 275 cm^{-1} .

Not much need be said regarding the records covering the range between 7μ and 13μ obtained with the comparatively thicker plates and reproduced as figures 1 to 6 in the text. The features exhibited by them will be readily understood in the light of the remarks made earlier. At 7μ , the absorption is that principally of the fifth-order due to the fundamental mode of highest frequency. This is readily observed in the record with the thickest plate (figure 1, 21 mm) but ceases to be noticeable with the smaller thicknesses. The absorption at 9μ which is of the fourth-order is quite evident in figures 1 and 2, is weak in figure 3, and ceases to be noticeable in the later figures of the series. The transmission between 9μ and 12μ becomes progressively more complete with diminishing thickness, as can be seen from figures 3, 4, 5 and 6. In the region between 12μ and 18μ , we observe another significant series of changes. The cut-off at 12μ due to the third-order absorption seen in figure 1 has disappeared in figure 2. It has, in fact, shifted to 18μ as can be seen from figures 7, 8 and 9. As the result of the increasing transmission at 12μ and the cut-off at 18μ , the drop in transmission between 12μ and 18μ becomes progressively steeper with diminishing absorption path. This is apparent in

figures 7, 8 and 9. In these figures, there is also a perceptible dip in the transmission curve in the wavelength range between $14\ \mu$ and $16\ \mu$. This may be identified as the effect of the second overtones of modes II and III listed in table 1. There are also indications of the absorption due to the first overtones of the same two modes in the wavelength range between $20\ \mu$ and $23\ \mu$ in figure 12.

Summary

Twelve spectrophotometer records of the absorption by NaF plates are reproduced covering the wavelength range between $7\ \mu$ and $23\ \mu$ for absorption paths ranging from 21 mm down to 0.18 mm. The octave of the fundamental mode of highest frequency records itself as a sharply-defined absorption at $18.2\ \mu$. This gives $275\ \text{cm}^{-1}$ as the fundamental frequency, in fair agreement with the theoretically computed value of $281\ \text{cm}^{-1}$. It also fits in with the observed infrared reflection maximum at $36\ \mu$.

Reference

1. Raman C V "The specific heats of the alkali halides and their spectroscopic behaviour" *Memoir No. 131 of the Raman Research Institute and Proc. Indian Acad. Sci.* **A56** (1962).

The infra-red behaviour of the alkali halides

SIR C V RAMAN

1. Introduction

X-ray diffraction techniques enable us to ascertain the distribution within the volume of a crystal of the atoms composing it. But the geometry of the structure cannot by itself form the basis for any valid deductions regarding the physical properties of the crystal. To enable any such deductions to be made, a knowledge of spectroscopic behaviour of the crystal is essential. By a careful investigation of a few particularly simple cases, the basic principles connecting structure and spectroscopic behaviour may be elucidated and established. Such an investigation has been carried out in the case of diamond which is accessible to spectroscopic study by a variety of methods. It will suffice here to refer to a recent memoir* by the author in which the infra-red absorption spectra of diamond have been described and explained in terms of its crystal structure. In an article which appeared in *Current Science* for October 1962, this work has been briefly summarised.

2. The alkali halides

Whereas diamond stands apart by itself as a crystal composed of atoms all of one kind which is favourable for spectroscopic investigation, we have in the alkali halides a whole family of crystalline solids which are accessible to study by well known spectroscopic methods. The fluorides, chlorides, bromides and iodides of the alkali metals lithium, sodium, potassium and rubidium (sixteen in all) have a similar structure. They exhibit a wide range of variation in their physical behaviour and for that very reason, are highly important as materials for study. In a recent memoir by the author**, an attempt has been made to deal with all these sixteen crystals from a unified standpoint and to establish connections between their spectroscopic behaviour and their physical properties. We may here briefly indicate the contents of that memoir.

Part I is a general introduction in which the physical constants of the sixteen

* The infra-red absorption by diamond and its significance. Memoir No. 129 of the Raman Research Institute; also *Proc. Indian Acad. Sci.*, A55, 1 (1962).

** The specific heats of the alkali halides and their spectroscopic behaviour. Memoir No. 131 of the Raman Research Institute; also *Proc. Indian Acad. Sci.*, A56, 1 (1962).

halides and especially their elastic moduli are tabulated. In part II, the nine modes of free vibration of the atoms in a crystal having the rock-salt structure are deduced and described. Parts III and IV contain further developments of the dynamical theory and contain expressions for the frequencies of the nine normal modes in terms of the interatomic force-constants. In part V it is shown how these frequencies may be numerically evaluated, if only as a first approximation. The results of the evaluation are tabulated in part VI. Parts VII, VIII and IX deal respectively with the specific heat problem, the infra-red behaviour of the crystal and the spectral shifts observed in light-scattering from first principles. Parts X, XI and XII give the results of the specific heat computations for all the sixteen halides and compare them with the experimental data in the cases for which they are available.

3. The spectrum of free vibrations

The dispersion, absorption, and reflection of infra-red radiation by a crystal are effects arising from the interaction of the electro-magnetic field in the radiation with the structural units composing the crystal. As a first step toward an understanding of these effects, it is necessary to consider the nature of the spectrum of the free or spontaneous vibrations of these structural units. We may deduce their modes and frequencies by the methods of classical mechanics. For this purpose, the atomic nuclei may be regarded as simple mass particles and the electronic clouds surrounding them as massless springs which hold the structure together. The relevant theory is fully set out in the memoir cited above and it is sufficient here to state the results to which it leads. It emerges that the vibrational mode of highest frequency of the structure is one in which the metal and halogen atoms oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described simply in terms of the crystal structure; four of the modes are oscillations of the cubic layers, while the other four modes are oscillations of the octahedral layers, the movement alternating in phase from layer to layer, and being either normal or tangential to those layers. Since the oscillations of the metal and halogen atoms may be either in the same phase or in opposite phases, we have four modes for the cubic layers and four modes for the octahedral layers, and hence eight in all. The oscillations of the metal and halogen atoms located in the same cubic layers would be coupled with each other. But the oscillations of the metal and halogen atoms appearing as distinct layers in the octahedral planes would be independent.

4. The mechanism of infra-red absorption

The absorption of infra-red radiation by a crystal implies the possibility of a transfer of energy from the field to the solid, a quantum of the energy of the

incident radiation being taken over and transformed into one, two or more quanta of vibrational energy in the crystal. The possibility of such a transfer arises from the interaction between the electromagnetic field of the radiation and the electric charges present in the structure of the crystal. These charges are of two kinds, viz., the positive charges of the massive atomic nuclei and the negative charges of the mobile electrons. These charges hold each other in place in the crystal structure as an ordered assembly. The roles which the positive and negative charges respectively play in the absorption of infra-red radiation have, therefore, to be discussed.

In all the modes of oscillation with which we are concerned, there are as many atomic nuclei moving in one phase as in the opposite phase, the respective amplitudes of oscillation being such that the centres of inertia of the structural units in the crystal remain at rest. Now, the ratio of the nuclear charges of sodium and chlorine is sensibly the same as the ratio of their atomic weights. As a result of this situation, the movements of the positive charges of the atomic nuclei when multiplied by their displacements and summed up would also cancel out. Hence, the forces exerted by the field on the positive charges in the structure cannot possibly set it in vibration. Thus, we are led to conclude that though the masses of the atomic nuclei appear in the expressions for the frequencies of vibration, the movements of the charges carried by them would not play any role in the infra-red activity of the crystal. Likewise, the movements of the negative charges carried by the electrons would not give rise to infra-red activity if it be assumed that each nucleus has associated with it the quota of electrons needed to neutralise its charge and that these electrons are carried along with it in its movements.

Thus we arrive at the following two conclusions. Firstly, the infra-red activity of the crystal owes its origin exclusively to the movements of the electrons and of the negative charges carried by them. Secondly, the electrons thus contributing to the activity are not those which are associated with any particular nucleus and participate in its movements, but are those electrons which enter into the structure of the crystal and whose movements are therefore determined jointly by movements of more than one nucleus. Infra-red activity can only arise if the displacements of electric charge thus resulting do not vanish when summed up each element of volume in the crystal. Though these results were derived with reference to the specific case of rock-salt, it could scarcely be doubted that they are of general validity.

5. The activity of the normal modes

Basing ourselves on the foregoing considerations, we can proceed to discuss the possibility of each of the nine normal modes described earlier being excited by incident radiation having the same frequency as the vibration. It is immediately

obvious that the mode of highest frequency in which the metal and halogen atoms oscillate against each other in opposite phases could be so excited. For, the movements of the negative charges set up by the movements of the two sets of nuclei, though opposite in phase, would be of unequal magnitude, and hence their resultant would not vanish. The surviving movement of charge could therefore enable the oscillation to be excited by the field. It is also evident that no such excitation would be possible in the case of the eight other normal modes. For, in these modes, the atomic nuclei of either species oscillate in opposite phases in the alternate layers of the structure, and hence the movements of negative electric charge resulting therefrom would cancel out when summed up over any individual volume element in the crystal.

We have next to consider the cases in which the frequency of the incident radiation is a multiple of the frequency of the normal mode under consideration and a quantum of energy of the field if taken up would be transformed to two, three or more quanta of vibrational energy in the crystal. For such excitation to be possible, the movements of electric charge resulting from the vibration should include a periodic component having the frequency of the field which does not vanish when summed up over an individual volume element in the crystal. Electrical anharmonicity associated with a finite amplitude of vibration is requisite for such an effect. It can evidently arise in the case of the vibrational mode which has the highest frequency and the maximum activity of all the modes. It is readily shown also that the coupled modes of vibration of the atomic nuclei in the cubic layers of atoms could be excited by a radiation which has *double the frequency* of the vibrational mode under consideration. *Per contra*, the symmetry characters of the modes of vibration of the atomic nuclei in the octahedral layers of the structure preclude any such excitation.

6. The infra-red absorption spectrum

The considerations set forth enable us in a general way to envisage the behaviour of the alkali halides in respect of the absorption of infra-red radiation. Some supplementary remarks are, however, necessary. By reason of the excitation of the normal modes by radiations having multiple frequencies, the absorption spectrum would extend to much smaller wavelengths than the spectrum of free vibrations of the structure. The strength of the absorptions of higher orders may however be expected to fall off rapidly with the increasing order. Further, the finite amplitudes of vibration excited by the radiation would necessarily involve besides electrical anharmonicity, also a mechanical anharmonicity of the vibrations, and this in its turn involves other consequences. The several normal modes of vibration can no longer be considered as being completely independent of each other or as being strictly monochromatic in their frequencies. Modes which are inactive when considered independently would be rendered active by

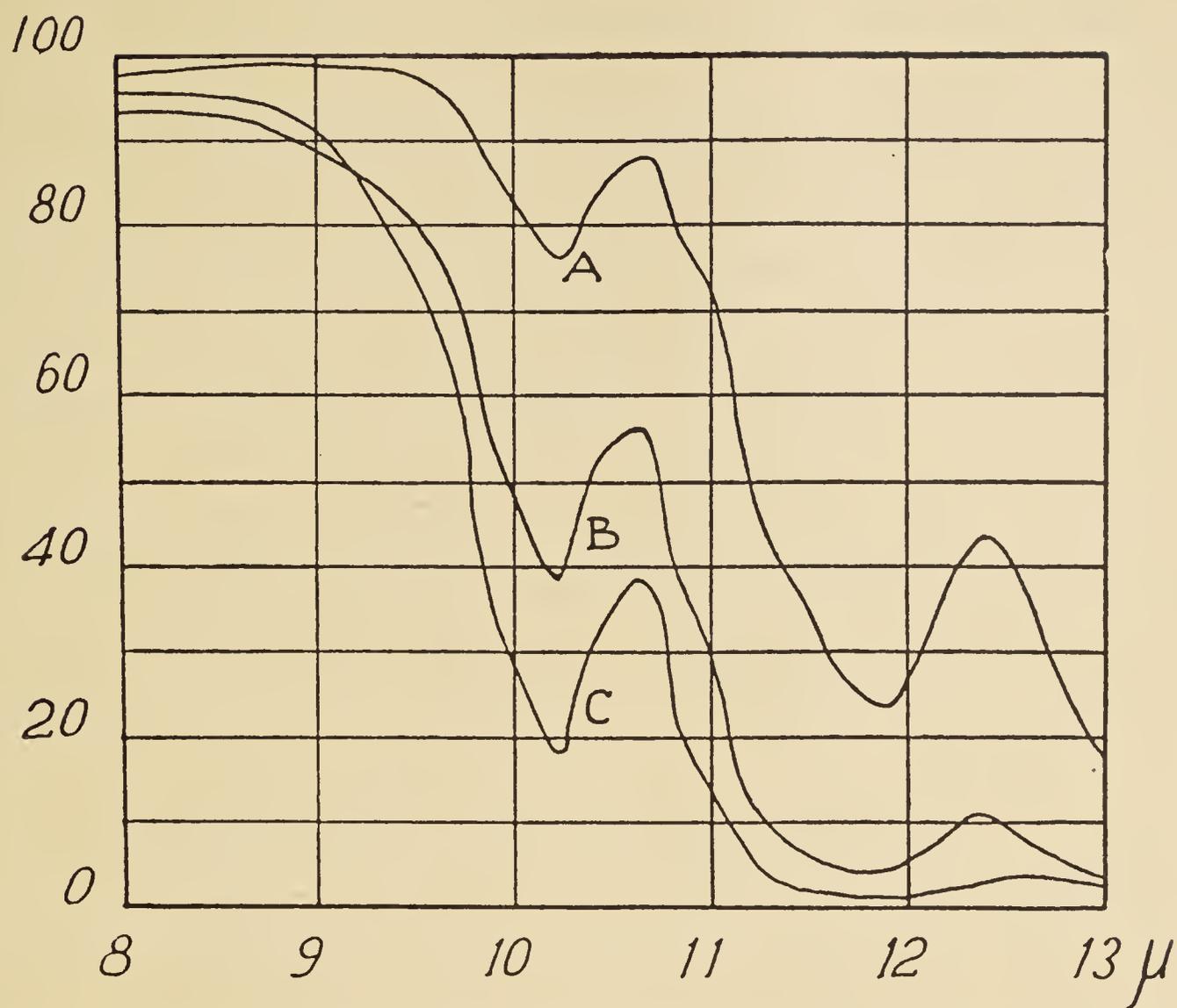


Figure 1. Magnesium oxide, infra-red transmission percentages. Plate thickness: A. 0.06 mm, B. 0.11 mm, C. 0.28 mm.

reason of their contiguity in frequency to other active modes of vibration. In particular, the principal and most strongly active mode having the highest frequency would influence all the other eight modes of lower frequency and render them active to varying extents depending on the differences of their frequencies from that of the mode of highest frequency.

It will be evident from all that has been said above that the characters of the spectrum of free vibrations could by no means be expected to manifest themselves very conspicuously in the spectrum of infra-red absorption. We have indeed to investigate the behaviour in the transmission of infra-red rays pretty thoroughly using plates of various thicknesses ranging from the largest to the smallest practicable values to enable us to disentangle the various normal modes and their overtones from each other and demonstrate the relationships between the possible free vibrations of the structure and their manifestation in the spectrum of infra-red absorption. Such investigations have been carried out by the author and the results have been presented in a series of memoirs dealing with several individual cases.

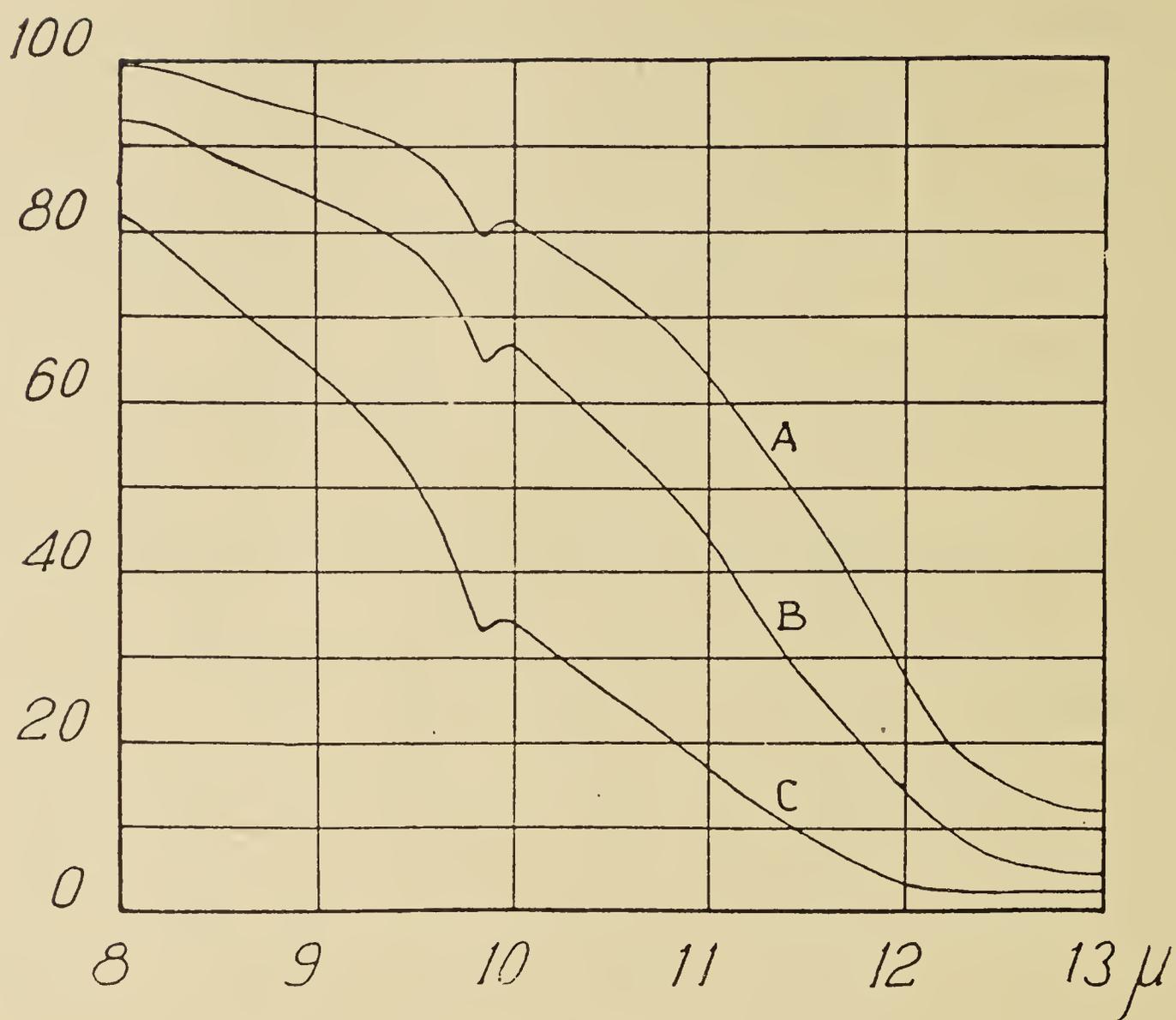


Figure 2. Lithium fluoride, infra-red transmission percentages. Plate thickness: A. 0.10 mm, B. 0.15 mm, C. 0.28 mm.

A Leitz infra-red recording spectrophotometer was available which was provided with both NaCl and KBr optics, the former covering the wavelength range between 1μ and 15μ and the latter the range between 13μ and 24μ . The materials investigated can be classed into three groups. The first included the alkali halides NaCl, KCl, KBr and KI commonly used as dispersing prisms for infra-red spectroscopy. Their characteristic wavelengths appear in the remote infra-red. The second group consisted of MgO and LiF whose characteristic wavelengths lay within the range of the KBr optics. Though MgO is not an alkali halide, its structure is similar to that of rock-salt and very significant results were obtained with it. The third group comprised the crystals NaF and CaF_2 . Their characteristic wavelengths lay beyond the range of the KBr optics, but the records obtained in that range exhibited very significant features. Though the structure of CaF_2 differs from that of the alkali halides, the results obtained with it present some interesting points of comparison with LiF and NaF.

7. The spectrophotometric results

The observational data for the cases of MgO, LiF, NaF, CaF₂ and for NaCl have been set out fully in the individual memoirs dealing with these materials*. As is naturally to be expected in view of the diversity in the sizes and masses of the combining atoms and of the strength of their binding in these crystals, special features characteristic for each individual material are noticeable in the spectrophotometric records which have been reproduced in the memoirs, and these features are indeed highly significant. Nevertheless, it is possible to trace certain other features common to all the cases studied and which are to be expected in the light of the theoretical considerations set out above. To illustrate these differences and similarities, some of the records for the different thicknesses of the same materials have been grouped together and are reproduced here as figures 1, 2, 3 and 4 in the text. These refer respectively to the cases of MgO, LiF, NaF and CaF₂, and are the records obtained with the thinnest plates made use of in their cases.

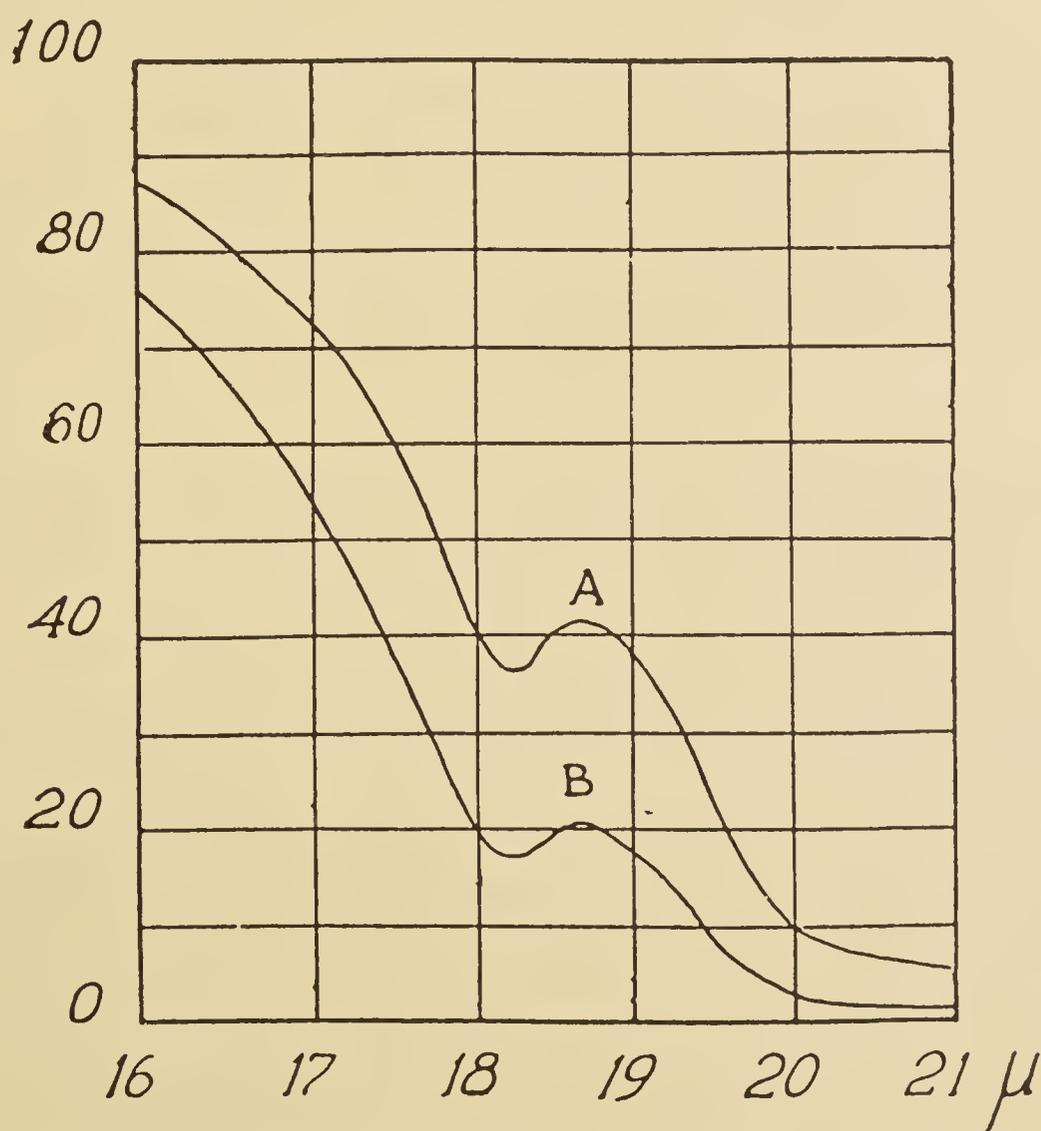


Figure 3. Sodium fluoride, infra-red transmission percentages. Plate thickness: A. 0.18 mm, B. 0.36 mm.

*Memoirs of the Raman Research Institute, Nos. 127, 130, 132, 134 and 128—*Proc. Indian Acad. Sci.*, A54, 205 (1961); A55, 131 (1962); A56, 223 (1962); A56, 291 (1962); A54, 253 (1961).

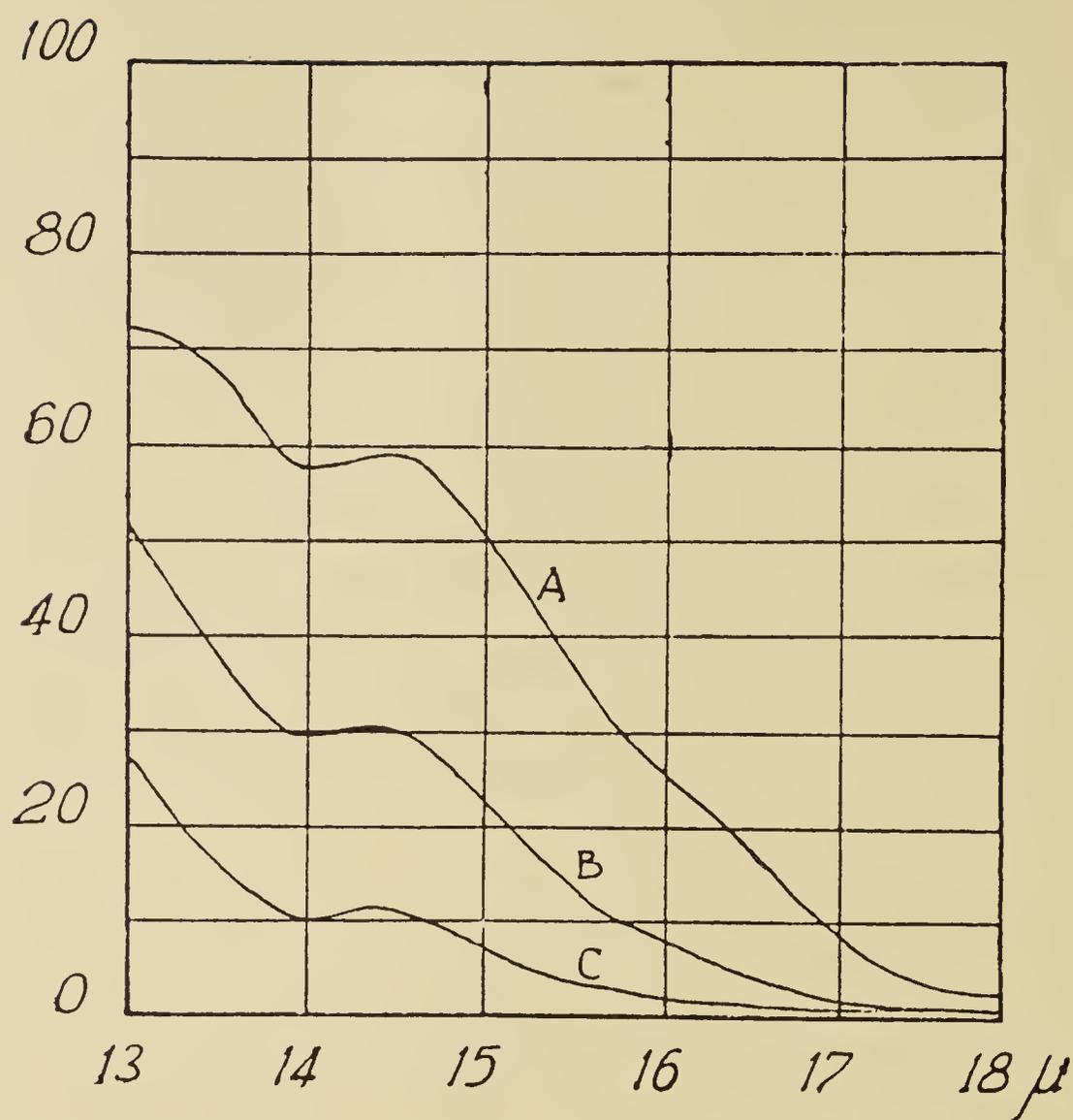


Figure 4. Calcium fluoride, infra-red transmission percentages. Plate thickness: A. 0.11 mm, B. 0.25 mm, C. 0.43 mm.

Attention may be drawn to the very steep drop in transmission noticed between 9μ and 10μ in each of the three curves reproduced in figure 1 for MgO. This drop is immediately followed by a sharply defined minimum of transmission at 10.20μ . A similar but less steep fall between 8μ and 9.8μ is noticed in figure 2 for the case of LiF and this is followed by a shallow but sharply defined dip at 9.84μ . Likewise in figure 3, referring to the case of NaF, we notice a steep fall of transmission between 16μ and 18μ and this is followed by a well-defined minimum at 18.2μ . In all the three cases, the steep drop represents the change in the infra-red absorption due to the mode of highest frequency from the third-order to the second-order, and the observed minimum of transmission represents the wavelength corresponding to the octave of the fundamental frequency. We are thus enabled to determine the latter accurately from the spectrophotometric records. The dip at 14μ noticed in all the three curves reproduced in figure 4 for CaF_2 is likewise identifiable as due to the octave of the mode of vibration in which the calcium atoms oscillate in one phase and the fluorines oscillate together in the opposite phase, resulting in a strong infra-red absorption.

The dynamics of the fluorite structure and its infra-red behaviour—Part I. Introduction

SIR C V RAMAN

Memoir No. 134 of the Raman Research Institute, Bangalore-6

Received October 30, 1962

Calcium fluoride (CaF_2) crystallises in the cubic system and is found widely distributed in nature as the mineral known by the name of fluorspar or fluorite. This is a material of great economic importance which is much sought after, the world production at the present time being of the order of a million tons per annum. Fluorspar has many industrial applications, the major uses being as a flux in metallurgy and as the source for the manufacture of hydrofluoric acid and therefrom of a great number of organic and inorganic fluorine compounds. The mineral itself as found in nature exhibits several highly interesting properties. It crystallises beautifully, usually as cubes and also sometimes as octahedra. Indeed, fluorite specimens are some of the most attractive exhibits to be found in mineralogical museums, by reason of the large size of the individual crystals, their grouping together as interpenetration forms and as clusters adhering to the matrix from which they emerged, and also by reason of the varied colours which they present. The luminescence which fluorspar exhibits under the ultra-violet lamp adds further to the interest of the material as a subject for study and research.

The origin of the striking colours often exhibited by the mineral fluorite is a problem in itself. Closely related to this is the problem of explaining the enormous variations in the intensity of the luminescence exhibited by the natural material under ultra-violet illumination. Indeed, the correlation between the colour of the fluorspar and the intensity of its luminescence is in many cases so obvious that it could scarcely be doubted that the two properties are interrelated. Particularly significant is the fact that the variations in the colour and the luminescence often appear side by side in the same specimen as bands or layers running through the material. Noteworthy also is the remarkable constancy of the density and refractivity of fluorspar despite the variations in the colour displayed by it. All these features taken together make it extremely unlikely that the variations in colour and the intensity of the luminescence displayed by fluorspar are ascribable to variations in its chemical composition. Indeed, it does not appear that any such variations have been established by chemical analysis.

In the present memoir, we shall concern ourselves with the infra-red behaviour of colourless fluorite. Specimens of such fluorite are not altogether uncommon in the natural deposits of the mineral, and in former times were much sought after by reason of their usefulness in the optical industry where components of low refractive index or with a high degree of transparency in the ultra-violet were needed. At the present time, such needs are filled by synthetically prepared crystals of optical quality. The procedure by which such crystals are grown is well known, viz., by melting the carefully purified material in the platinum crucible and subsequent slow solidification as the result of which it emerges from the crucible as a cylindrical casting with one end conical. Castings as large as 150 millimetres in diameter and 125 millimetres tall, weighing over 8 kilograms have been successfully prepared by this technique, the apex angle of the cone being 120° . From the material thus obtained, the forms in which it is actually needed for optical purposes, viz., windows, prisms and lenses, are cut out and prepared by appropriate techniques.

Some of the physical properties of fluorite may be usefully recalled here. The refractivity of the material is very low, the index for yellow light is 15°C being 1.4339. The dispersion in the visible region of the spectrum is also small but improves as we proceed into the ultra-violet, the refractive index attaining the value 1.50 at the wavelength $0.2\ \mu$. The transparency of fluorite in layers of moderate thickness however extends further into ultra-violet being quite good at $0.15\ \mu$ and sensible even at $0.125\ \mu$.

Prisms of synthetic fluorite are made use of for infra-red spectroscopy in the range of wavelengths between about $4\ \mu$ and $8\ \mu$. At wavelengths smaller than $4\ \mu$, the dispersive power of the material is too small to give adequate resolution, while at wavelengths greater than $8\ \mu$, its absorptive power is so large as seriously to interfere with the usefulness of the material as a dispersing medium. It is worthy of remark the wavelength $8\ \mu$ is far removed from the spectral region ($\sim 30\ \mu$) in which the reflecting power of the surface of a fluorite crystal reaches high values.

Fluorite is practically insoluble in water. Its melting point is 1360°C being much higher than those of lithium and sodium fluorides. The strength of the binding between the metal and halogen atoms indicated by these facts is also shown by the elastic behaviour of the crystal. The bulk-modulus $K = 8.78 \times 10^{11}\ \text{erg/cm}^2$, and the shear-modulus $C_{44} = 3.58 \times 10^{11}\ \text{erg/cm}^2$. These may be usefully compared with the corresponding figures for lithium fluoride ($K = 6.99$ and $C_{44} = 6.35$) and for sodium fluoride ($K = 4.85$ and $C_{44} = 2.80$). It will be noticed that the bulk-modulus of fluorite is the highest of the three, while its shear-modulus is intermediate between those of the other two. Both moduli are however far greater than those of the other alkali halides having the rock-salt structure. The densities of LiF, NaF and CaF_2 are respectively 2.60, 2.79 and 3.18. The differences between them appear small in view of the enormous differences in the atomic weights of the three elements, Li, Na and Ca, viz., 6.9, 23 and 40 respectively. But they become intelligible when the differences in crystal spacing

are considered. For, LiF, NaF and CaF_2 these are respectively 4.01 Å, 4.62 Å and 5.45 Å respectively.

As is well known, the crystal structure of CaF_2 presents a closer resemblance to that of diamond than to that of rock-salt. CaF_2 also resembles diamond in having a very perfect octahedral cleavage. The calcium atoms in fluorite are located at the corners and at the face-centres of the unit cubes of its structure, while the fluorine atoms are located at the centres of the eight cubes into which the unit cube may be subdivided. Thus, each fluorine atom in the structure is surrounded by four calcium atoms to which it is held by bonds parallel to the tetrahedral axes of the structure. Each calcium atom is held similarly to eight fluorine atoms, the calcium atom and the two fluorine atoms on either side of it being in the same line. The locations of the metal and halogen atoms with respect to each other thus differ from what we find in the alkali halides. The fluorines and the calciums appear in distinct layers both in the cubic and in the octahedral planes of the structure. In the cubic planes, the chlorine atoms and the fluorine atoms appear in equidistant layers whose separation is one-fourth the edge-length of the unit cubes, the fluorine layers containing twice as many atoms as the calcium layers. In the octahedral layers, each calcium layer has two fluorine layers one on either side of it, at a distance equal to one-eighth of the length of the body-diagonal of the cube. The pattern of three layers thus constituted repeats itself at intervals of one-third of the length of the body-diagonal.

Summary

The properties of fluorite, both as observed in the naturally occurring mineral and as exhibited by the synthetically prepared crystals, are briefly described and discussed.

The dynamics of the fluorite structure and its infra-red behaviour—Part II. The free modes of vibration

SIR C V RAMAN

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A consideration of the possible free modes of vibration of the atoms in a crystal about their positions of equilibrium is, of necessity, the starting point in the theory of its specific heats and also for an understanding of its spectroscopic behaviour. We are concerned to discover the nature of the movements of the massive positively charged nuclei about the locations in which they are held in the crystal by the clouds of the mobile negative charges which surrounds and encompass them. A practicable approach to the problem is that based on the principles of the classical mechanics.

A well known theorem states that all the possible small vibrations of a conservative dynamical system about a position of stable equilibrium may be represented as a superposition of certain modes of vibration designated as the normal modes of the system. The number of normal modes is equal to the number of degrees of dynamical freedom of the system, and in each such mode, the particles of the system execute harmonic vibrations with common frequency characteristic of the mode and their phases are all the same or opposite, in other words, they all pass simultaneously through their positions of equilibrium. It should be emphasised that this identity or opposition of phase is a fundamental feature of the normal modes. In the absence of such a phase-relationship, the possible movements of the particles would be infinitely varied and hence incapable of enumeration.

We have thus to answer the following questions. Do the atoms located in the structure of the crystal possess any normal modes of vibration having the stated characters? If so, what is the number of such modes and how is their number related to the number of atoms comprised in each unit cell of the structure? To find the answer to these questions, we make use of the fundamental property of a crystal that its structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Since each atom comes into coincidence with an equivalent atom in the next cell, all physical properties of the crystal determined by the atomic locations and the atomic interactions should also remain unaltered. It follows as a necessary consequence of this

situation that a vibration having the characters of a normal mode should continue to be a normal mode following a unit translation. This can evidently happen in two ways. Equivalent atoms brought into coincidence can have identical amplitudes and phases of vibration. Alternatively, their amplitudes can be the same but all the phases are reversed. (In the latter case, the original phases are regained after a half-period and hence the normal mode is effectively unaltered.)

The two alternative possibilities indicated above arise in respect of a unit translation along each of the three axes of the lattice. Since these are independent of each other, we have $2 \times 2 \times 2 = 8$ different possibilities in all. In each of these 8 possibilities, the amplitudes of vibration of the atoms in the cells adjoining a particular cell are the same as those of the equivalent atoms in that cell. Hence, if there are n atoms in each unit cell of the structure, their $3n$ equations of motion involving their interactions with the surrounding atoms which are assumed to be proportional to their relative displacements contain only $3n$ displacement co-ordinates. Hence the equations of motion can be completely solved, the solutions obtained giving us the frequencies and the ratios of the atomic displacements along each of the co-ordinate axes.

Considering all the eight possibilities referred to above, we have $8 \times 3n = 24n$ distinct solutions or normal modes of vibration. In $3n$ of these modes, the vibrations of equivalent atoms have the same phase in the adjoining cells, while in the remaining $21n$ modes, they appear with alternating phases along one or two or all three axes of the lattice. By the nature of the case, however, 3 out of the $3n$ modes have a zero frequency, in other words, represent simple translations. Hence we have only $(3n - 3)$ normal modes properly so-called of the first species and $21n$ normal modes of the second species.

The fluorite structure can be described as the result of the interpenetration of three similar rhombohedral (= face-centred cubic) lattices, one of calcium atoms and two of fluorine atoms. Hence, in what has been stated above, we have $n = 3$, and the number of normal modes of vibration of the first species is, therefore, 6 and of the second species is 63. The number of distinct frequencies of vibration would however be far smaller, by reason of the cubic symmetry of the entire structure and consequent degeneracy of the modes of vibration. The actual number of such frequencies and the modes of vibration exhibiting them can be readily derived in the following manner. We begin by considering the possible modes of vibration of each of the three lattices of atoms with which we are concerned. The eight possible alternatives regarding the relative phases of the atomic vibration in any one lattice give rise to 24 possible types of movement listed in a table on next page.

In the modes listed as (2), (3), (4) and (5), the oscillations alternate in phase as we proceed from layer to layer. The directions in which the layers of atoms oscillate, viz., normal or tangential as the case may be, are fixed by the symmetry of the structure. The symmetry also determines the degeneracies shown against the

Description of the modes	Degeneracy
1. Simple translations	3
2. Oscillations normal to the cubic planes	3
3. Oscillations tangential to the cubic planes	6
4. Oscillations normal to the octahedral planes	4
5. Oscillations tangential to the cubic planes	8
Total	24

respective modes. The free modes of vibration of the fluorite structure would evidently be superpositions of the movements or oscillations of the three lattices, these being geometrically similar but with amplitudes and phases relative to each other which are dynamically permissible. Taking first the simple translations of the three lattices, one of them reduces to a simple translation of all the three lattices together, and the other two give us the modes of oscillation pictured in figures 1 and 2 below respectively, each of which is three-fold degenerate. In the oscillation pictured in figure 1 the calcium atoms all move together in phase, while the fluorine atoms move together in the opposite phase. In the oscillation pictured in figure 2, the calcium atoms remain at rest, but the fluorine atoms oscillate with the two lattices in opposite phases.

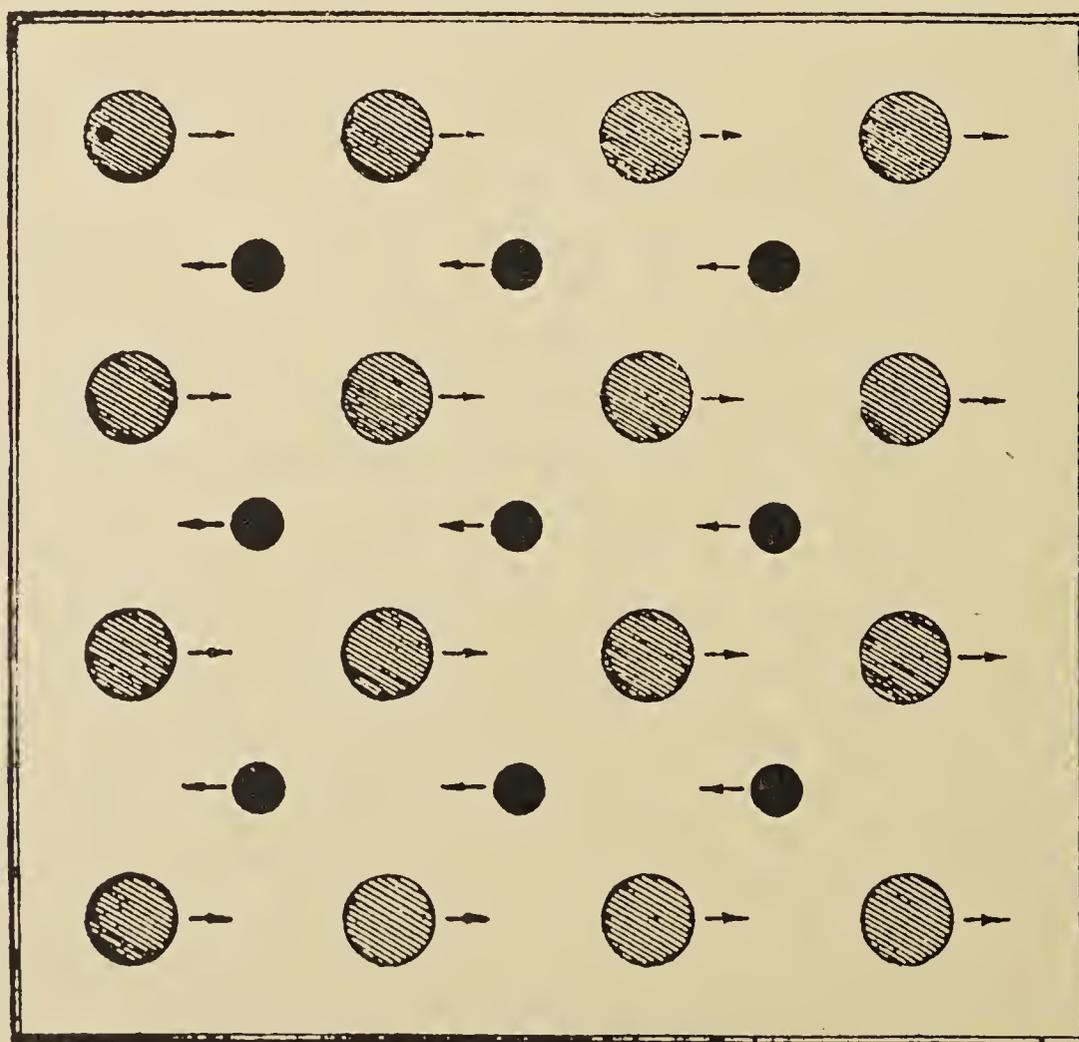


Figure 1. Oscillation of the calciums against the fluorines.

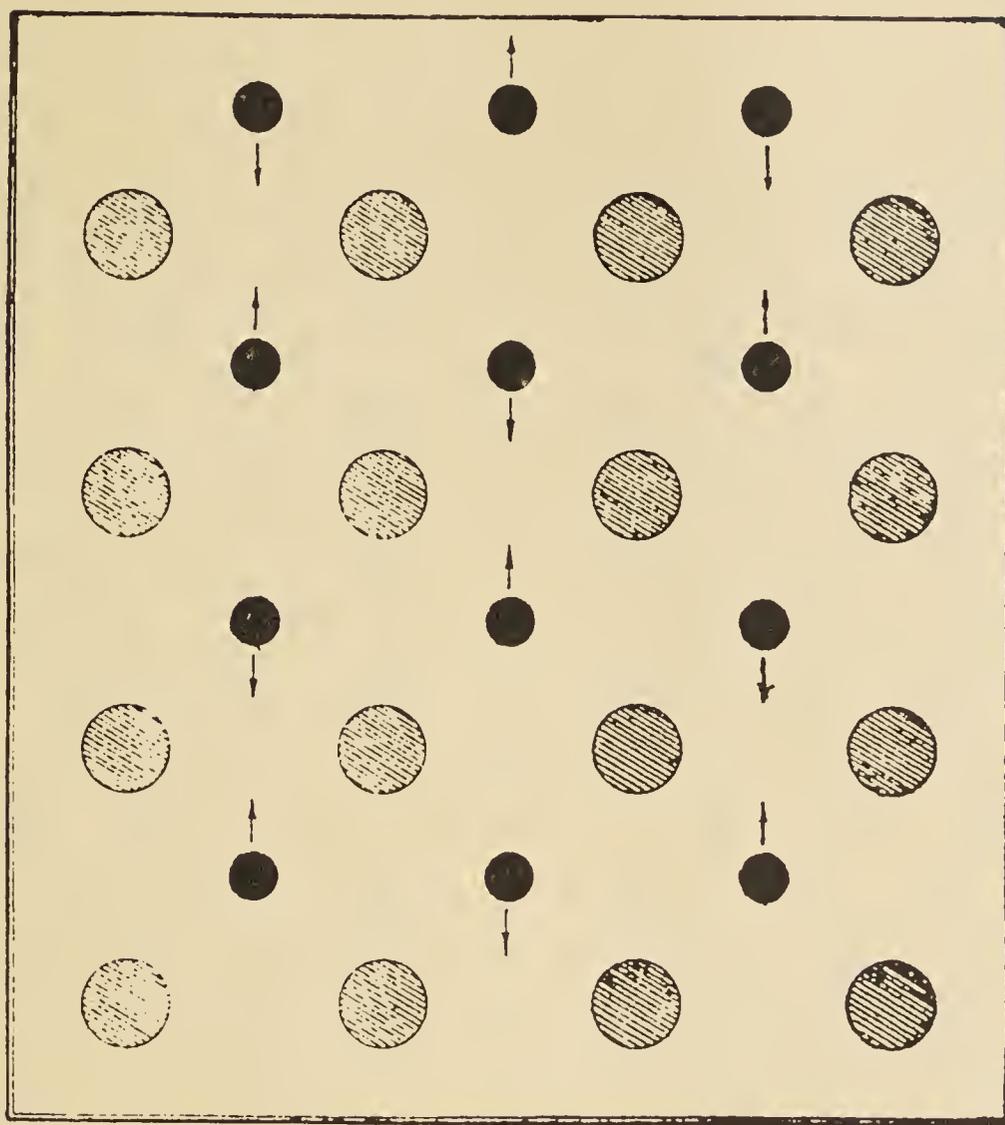


Figure 2. Oscillations of the fluorine atoms with the two lattices in opposite phases.

Likewise, the mode of oscillation of the cubic layers of atoms normal to themselves listed as (2) in the table resolves itself into three modes. In one of them, adjoining layers of fluorine and calcium atoms move in opposite phases. In another, they would move in the same phase. In the third mode, the calcium atoms would remain at rest and the layers of fluorine atoms would oscillate against each other. These three modes of vibration are shown diagrammatically in figures 3(*a*), (*b*) and (*c*) respectively. Each of these modes would have a degeneracy of 3. The corresponding modes of oscillation tangential to the cubic layers are shown diagrammatically in figures 3(*d*), (*e*) and (*f*). Each of them would have a degeneracy of 6.

The oscillation of the octahedral layers normal to themselves listed as (4) in the table would likewise divide up into three modes. In one of them, the three adjacent layers containing the calcium and fluorine atoms would move together in the same phase, the phase of all the three together reversing from one set of three layers to the next set. In another mode, the fluorine layers would move together in one phase and the calcium layers intermediate between them in the opposite phase. This movement again would reverse its phase in the next adjacent set of layers. In the third mode, the fluorine layers alone would oscillate in

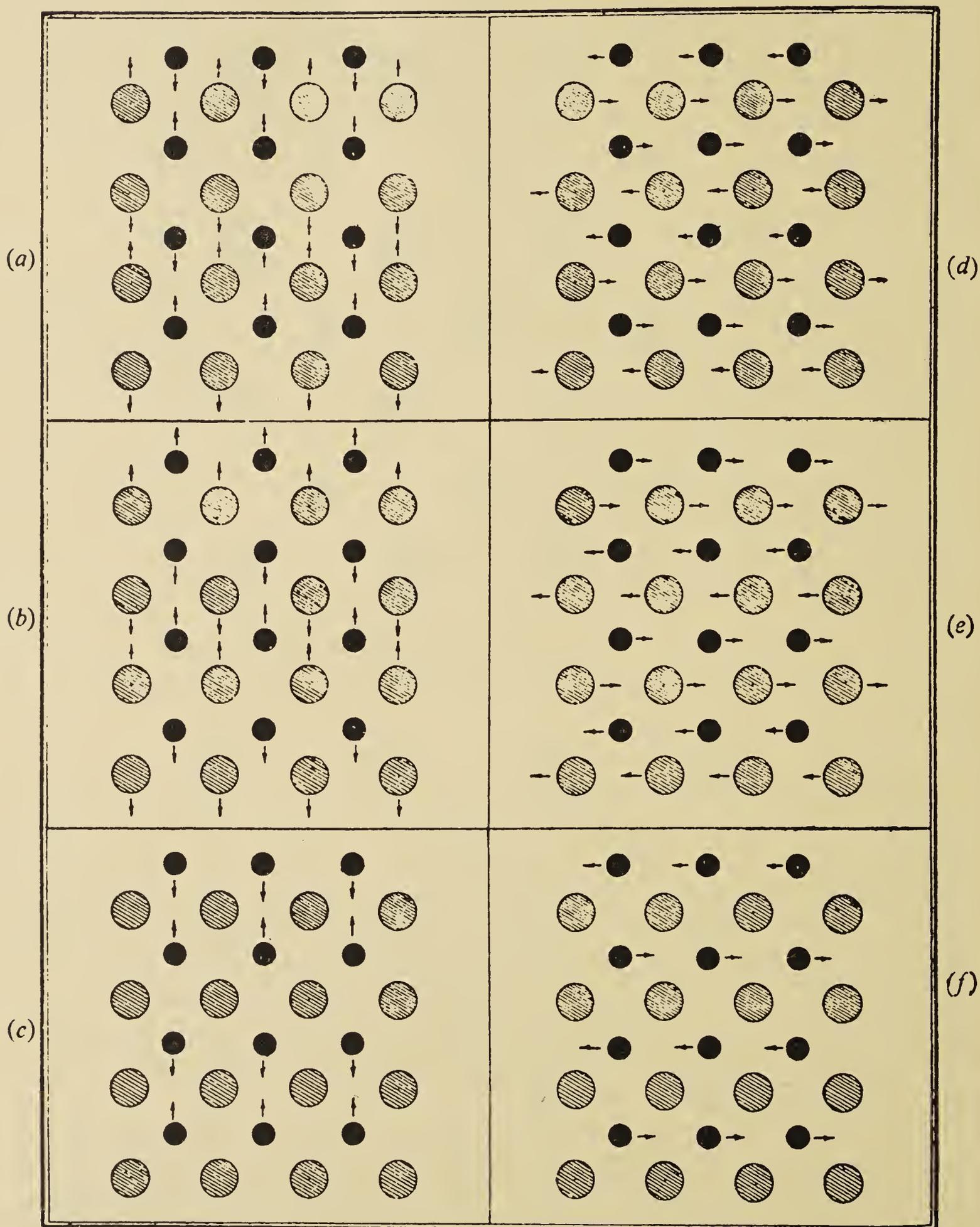


Figure 3. (a), (b), (c), (d), (e) and (f): Oscillations of the cubic layers of atoms.

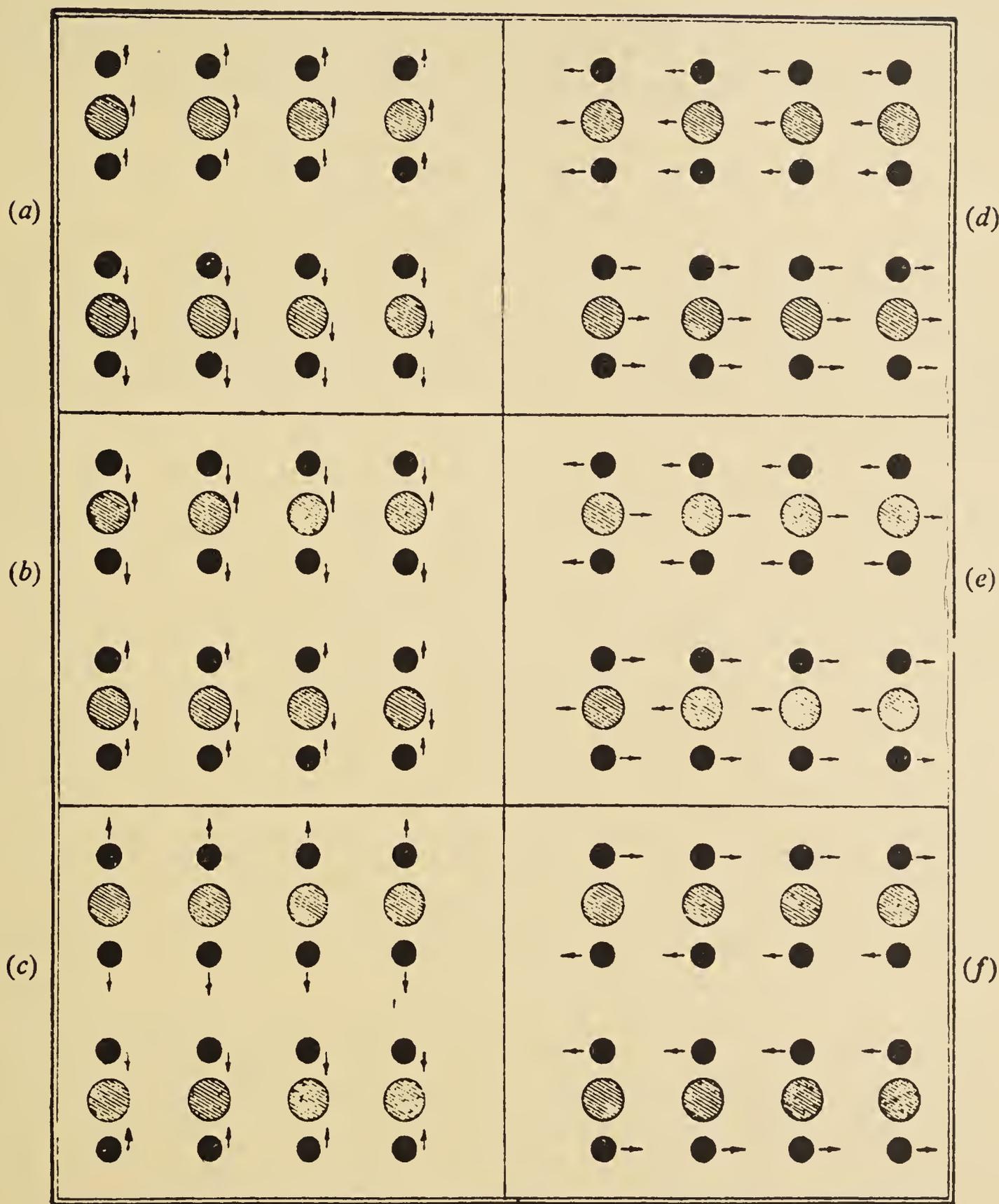


Figure 4. (a), (b), (c), (d), (e) and (f): Oscillations of the octahedral layers of atoms.

opposite phases, the intermediate calcium layer remaining at rest. This movement again would reverse in phase as we pass from one set of three layers to the next. Each of these three modes would have a degeneracy of 4. They are represented in figures 4(*a*), (*b*) and (*c*) respectively. The three corresponding tangential modes are represented in figures 4(*d*), (*e*) and (*f*). They have each a degeneracy of 8. The degeneracies of all the fourteen normal modes when summed up give 69 to which, on adding the three omitted translations, we obtain 72 as the total.

Summary

It is shown that the fluoride structure has 14 different frequencies of vibration corresponding to the same number of normal modes with degeneracies of 3, 3, 3, 6, 3, 6, 3, 6, 4, 8, 4, 8, 4 and 8, besides three translations, making up a total of 72 degrees of freedom. The normal modes have been described and represented diagrammatically.

The dynamics of the fluorite structure and its infra-red behaviour—Part III. Activity of the normal modes

SIR C V RAMAN

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In the preceding part of the memoir it has been shown that the fluorite structure has fourteen different monochromatic frequencies of vibration. Two of these may be designated as the principal frequencies, since the vibrational modes repeat themselves in adjoining cells of the structure without change of phase. The remaining twelve may be referred to as the subsidiary frequencies, since in these vibrations, the phase of the vibration is reversed as we pass from cell to cell along one, two, or all three axes of the structure. For an evaluation of the thermal energy of the crystal as a function of the temperature, as also for a complete determination of its spectroscopic behaviour, a knowledge of all the fourteen frequencies is necessary. For the theoretical evaluation of these frequencies to be possible, the force-constants which determine the magnitude of the interactions between neighbouring atoms arising from their relative displacements should be known. Since, however, our immediate purpose is the interpretation of the observed spectroscopic behaviour of the crystal, the problem of evaluating the frequencies will be deferred for later consideration and we shall proceed to discuss the activities of the fourteen different normal modes, in other words, the possibility of their revealing themselves in various methods of spectroscopic study.

It is evident that the principal mode of vibration pictured in figure 1 of the second part of this memoir would play the major role in the infra-red activity of the crystal. For, in that mode, the calcium atoms move together in one phase and the fluorine atoms move together in the opposite phase and the movement repeats itself from cell to cell of the structure. These movements of the calcium and fluorine atoms would disturb the distribution of the negative electric charge in the cells of the structure and result in a periodic displacement of negative charge which does not vanish when summed over the volume of each unit cell, and therefore also over any small volume-element of the crystal. This movement of electric charge would enable the electric field of the infra-red radiation incident on the crystal to react with it and transfer energy to it, the energy-quanta of the incident radiation being taken over by the crystal as one, two, three or more

quanta of vibrational energy. Hence, the mode of vibration referred to would result in an absorption of the incident radiation in its spectral region corresponding to its fundamental frequency and also to multiples of that frequency; the absorption would thereby manifest itself in a succession of regions whose wavelengths form a harmonic progression. The possibility of the overtones of the fundamental frequency thus manifesting themselves in absorption arises by reason of the finiteness of the amplitudes of the vibration in the unit cells of the structure excited by the incident radiation. It is, therefore, to be expected that the absorption would fall off rapidly in strength as we go up the series of overtones to higher frequencies and thus towards smaller wavelengths in the spectrum.

We proceed to consider the second principal mode of vibration which is an oscillation of the two lattices of fluorine atoms against each other in opposite phases, the calcium atoms remaining at rest. It is evident that such an oscillation, considered as an independent mode of vibration, would be totally inactive in the absorption of infra-red radiation. For, the displacements of electric charge on either side of every calcium atom resulting from the movements of the fluorine atoms belonging to the two lattices would be in opposite senses and would therefore cancel out when summed up. Such cancellation would be effective not only as a first approximation but also in the higher approximations.

The possibility of the frequencies of vibration corresponding to the two principal modes appearing as frequency shifts in the scattering of monochromatic light may be next considered. Such frequency shifts owe their origin to the periodic variations in the optical polarisability of the structural units of the crystal associated with their internal vibrations. It is clear that in this respect, the roles of the two principal modes of vibration would be quite different. The mode which is active in the absorption of infra-red radiation would be inactive in respect of the scattering of light with altered frequency. Vice versa, the mode which is inactive as an absorber of infra-red radiation would be active in light-scattering and would give rise to a frequency shift equal to its own frequency. It should be noted, however, that since the refractive index of fluorite and therefore also the optical polarisability is very low, the variations resulting from the internal vibrations would also be small. Hence, the intensity with which the active mode is recorded as a frequency shift would be low. In the second approximation, in other words, when the effect of the finite amplitudes of vibration is taken into account, both of the principal modes of vibration should be active in light-scattering and give rise to shifts of frequency which are double their natural frequencies. But in view of what has been stated above regarding the low scattering power of the fluorite structure, this possibility is not of much practical significance.

We may here content ourselves with a few remarks regarding the activities of the twelve subsidiary modes of vibration. These modes of vibration involve a reversal of phase from cell to cell of the structure along one, or two or all three axes of the structure. This excludes the possibility of their manifesting themselves either in the absorption of infra-red radiation or in the scattering of light in the

first approximation. In the second approximation, infra-red activity is allowed in respect of some of the modes and not permitted in respect of the others, the considerations which determine the appearance or non-appearance being the symmetry characters of the respective modes. Theoretically also, the twelve subsidiary modes can appear in the scattering of light with doubled frequency shifts and with intensities depending on the actual nature of the modes. But for the reasons already explained, this possibility is not of much practical significance.

Summary

It is shown that the first of the two principal modes of vibration is strongly active in the absorption of infra-red absorption both as a fundamental and as a series of overtones and that the other mode would be wholly inactive. The position is reversed in the scattering of light with shifts of frequency; the first mode is not allowed, but the second is permitted.

The dynamics of the fluorite structure and its infra-red behaviour—Part IV. The spectrophotometer records

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In the present part of the memoir, we shall reproduce and discuss a series of spectrophotometer records of the infra-red transmission by plates of fluorite, their thicknesses ranging from a maximum of 37 millimetres down to less than a tenth of a millimetre, the greatest absorption path being thus some 400 times smaller. An enormous range of absorptive powers is thus covered and displayed by the records.

Synthetically prepared fluorite of optical quality which is commercially available has been employed for obtaining the spectrophotometer records reproduced in this memoir. As is well known, such fluorite is prepared by melting chemically pure CaF_2 in a platinum crucible having a conical vertex and allowing it to solidify slowly. The material thus obtained is perfectly colourless and its transparency extends far into the ultra-violet. Specimens of natural fluorite have, however, also been investigated. With material of the best quality which is colourless, transparent and free from inclusions, the results do not differ noticeably from those recorded with the synthetic specimens.

Three specimens of synthetic fluorite from different sources were available for the studies. The first was a block of dimensions 37 mm \times 37 mm \times 9 mm supplied by a well known British firm. The second specimen was a fluorite window 25 mm \times 25 mm \times 1.52 mm gifted to the author by Dr E K Plyler of the National Bureau of Standards at Washington. The third specimen was a small plate 1.7 mm thick sent by Prof. R Mecke from his Institute at Freiburg. All records reproduced in the present memoir were made with the material of British origin, the plates of the requisite thickness being obtained by cutting, grinding and polishing. The specimens of American and German origin give records similar to those recorded with the British material and hence they have not been reproduced.

In all, some fifty records were made with twenty different absorption paths. With a plate thickness of a millimetre or more, there is a complete cut-off beginning at 13 μ and extending towards greater wavelengths. Hence with such plates the KBr optics is ineffective and only the NaCl optics could be used. The range between 13 μ and 15 μ is common to both the NaCl and the KBr optics.

Though there was a fair agreement between the results they recorded, the KBr results were clearly the more trustworthy. Hence the records made with the NaCl optics reproduced in the memoir exhibit only the transmission curves up to $13\ \mu$, while at $13\ \mu$ and greater wavelengths, only the records made with the KBr optics are shown. All the latter refer to absorption paths which are less than a millimetre.

An inspection of the nine figures reproduced in the text indicates that we are dealing with absorptions of an altogether different order of magnitude in the three wavelength ranges, $7\ \mu$ to $8\ \mu$, $9.5\ \mu$ to $10.5\ \mu$ and $13\ \mu$ to $17\ \mu$. We shall remark upon these separately.

$7\ \mu$ to $8\ \mu$.—There is a readily observable absorption in this region with the largest thickness employed, viz., 37 mm (figure 1). It has sensibly weakened when the path is reduced to 29 mm (figure 2); it is very weak with an absorption path of 11 mm (record not reproduced) and still weaker with a thickness of 9 mm (figure 3). It is nearly unobservable with a 4 mm path (figure 4).

$9.5\ \mu$ to $10.5\ \mu$.—A complete or nearly complete cut-off is exhibited in this region in figure 1 and figure 2, the absorption path being in these cases a few centimetres. When the thickness is reduced to about a centimetre, the wavelength of cut-off moves to $13\ \mu$ beyond which there is a complete opacity. The transmission between $9.5\ \mu$ and $10.5\ \mu$ then rapidly increases as the thickness is reduced. This is shown very clearly in the series of records, figure 3, figure 4 and figure 5. Finally, when the thickness is reduced to a fraction of a millimetre, the absorption between $9.5\ \mu$ and $10.5\ \mu$ becomes very weak or unobservable.

$13\ \mu$ to $17\ \mu$.—Nine different absorption paths ranging from 9 mm down to 0.09 mm were investigated. They exhibit a progressive increase in transmission between the wavelengths of $13\ \mu$ and $17\ \mu$ commencing from complete opacity at a thickness of one millimetre. Two very significant features are noticeable in the records. The transmission curve exhibits a dip at $14\ \mu$ which is conspicuous and well-defined. Its position remains unaltered as the thickness is progressively reduced to the smallest possible value determined by the fragility of the material. At the same time, the actual transmission at $14\ \mu$ increases progressively upto about 75%. It is thus clear that $14\ \mu$ is a characteristic wavelength for fluorite. The other feature is noticeable in the records for the two smallest thicknesses reproduced as figure 8 and figure 9 respectively. It will be seen that the transmission curve descends steeply beyond $14\ \mu$ and then takes a sharp turn after which it slopes down less steeply. The location of this turning point is quite definite, viz., $15.6\ \mu$ and remains unaltered as the thickness is diminished to the limit. Thus, we are led to recognize $14\ \mu$ and $15.6\ \mu$ as two characteristic wavelengths in the infra-red absorption spectrum of fluorite.

The facts of observation set forth above are readily understood when considered in the light of the theoretical ideas developed in the two preceding parts of the memoir. It was shown that the principal mode of vibration of the structure in which the calcium atoms and the fluorine atoms oscillate in opposite phases would be strongly active in the absorption of infra-red radiation, not only

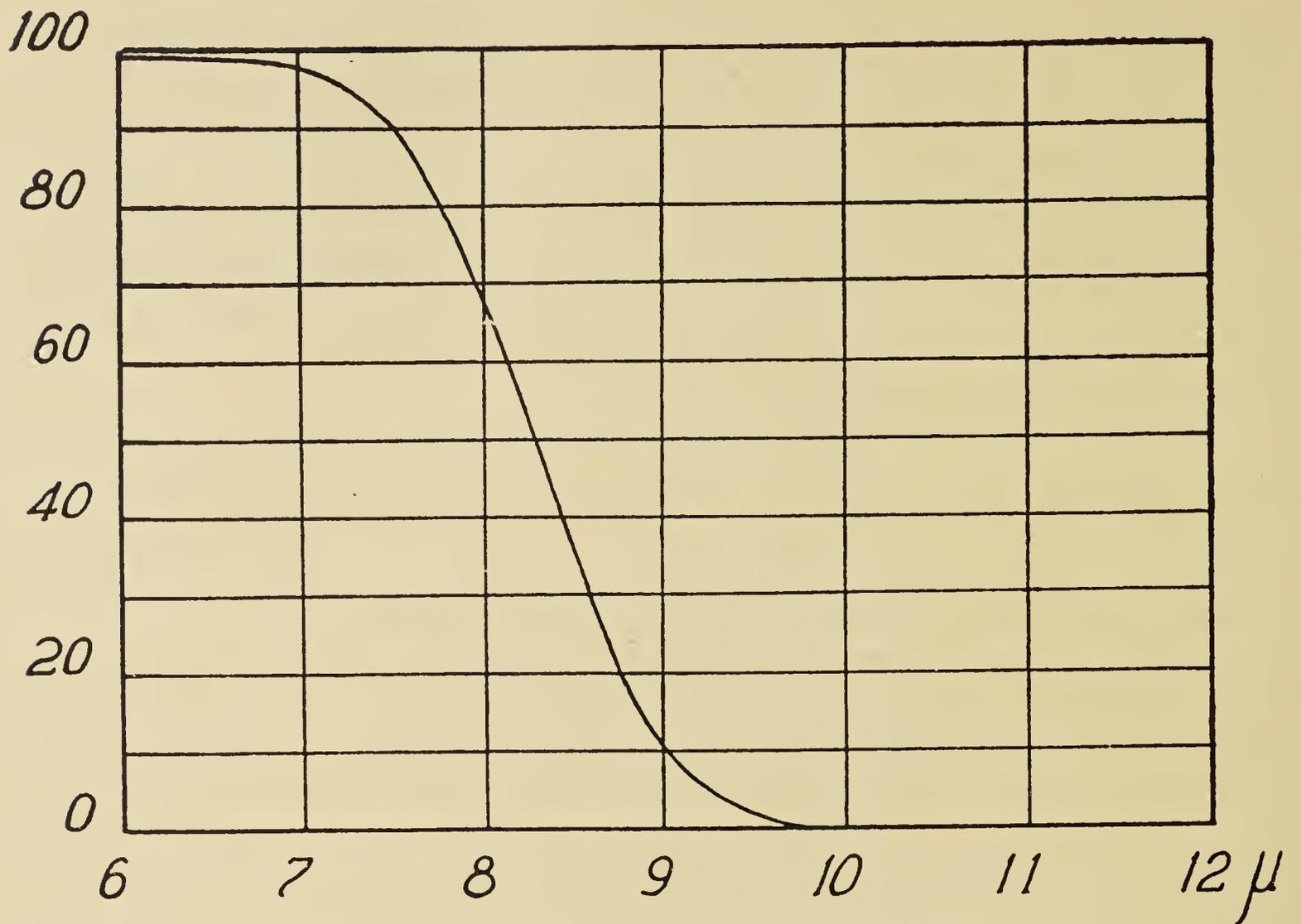


Figure 1. Transmission by fluorite; thickness 37 mm.

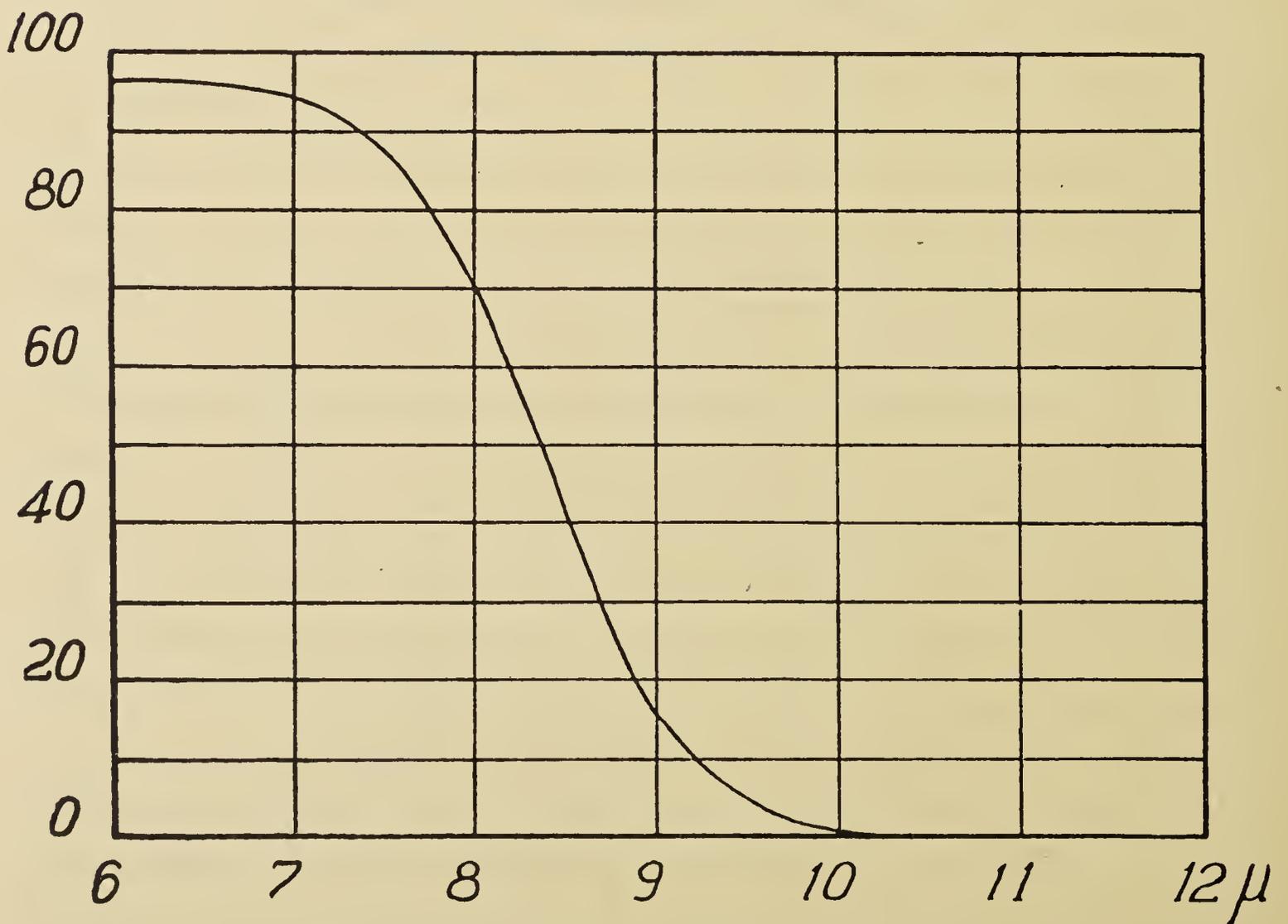


Figure 2. Transmission by fluorite; thickness 29 mm.

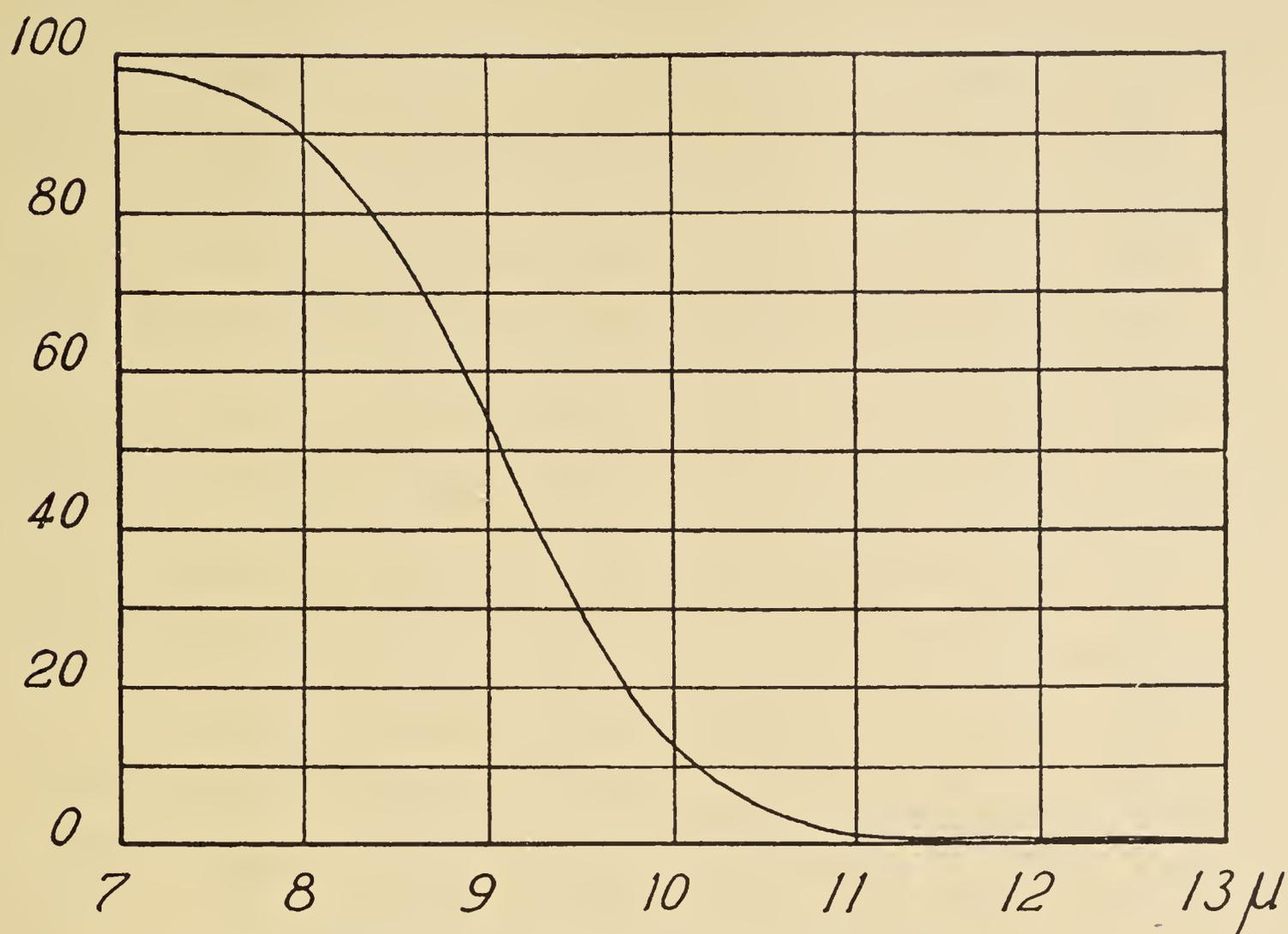


Figure 3. Transmission by fluorite; thickness 9 mm.

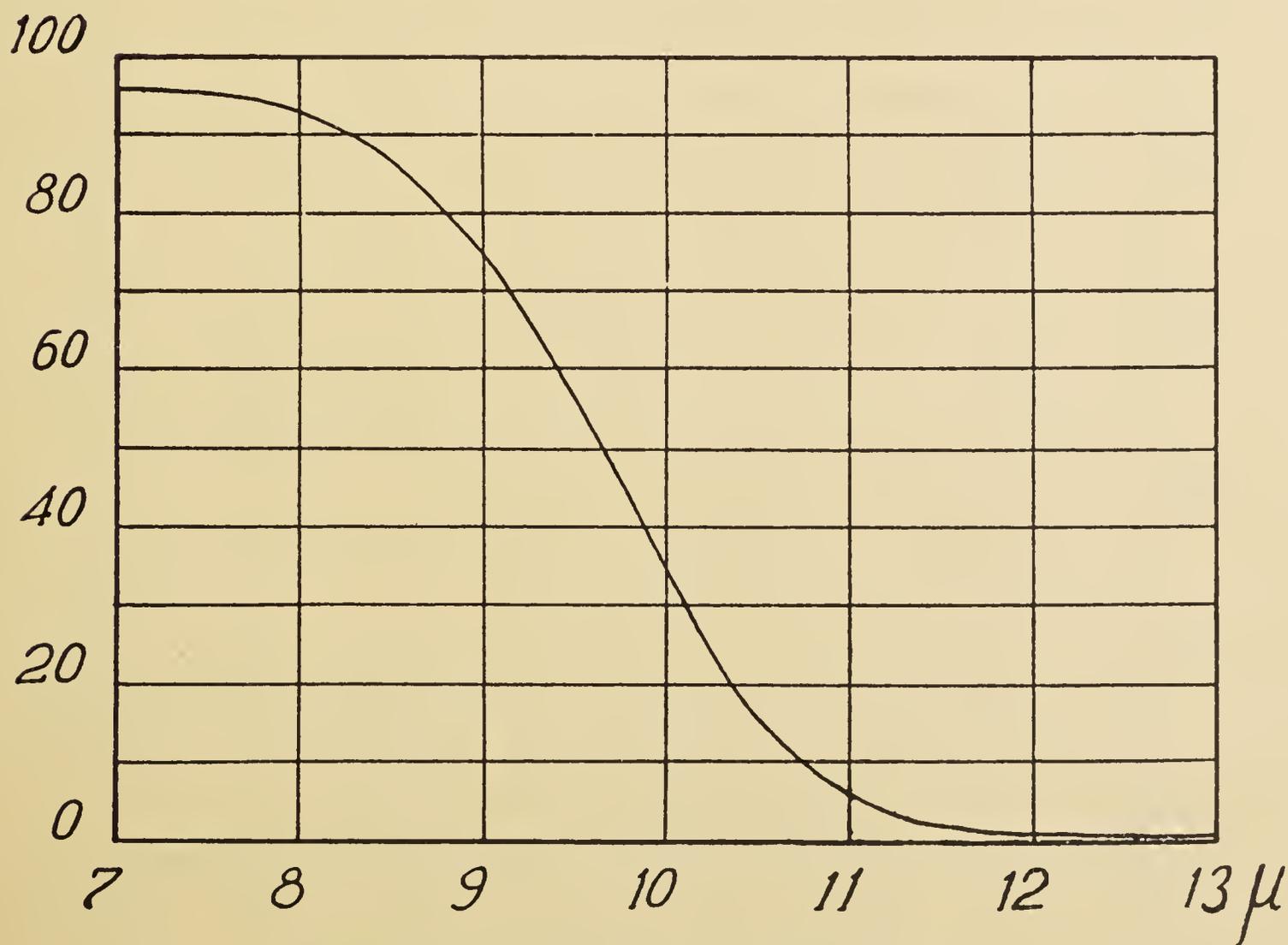


Figure 4. Transmission by fluorite; thickness 4 mm.

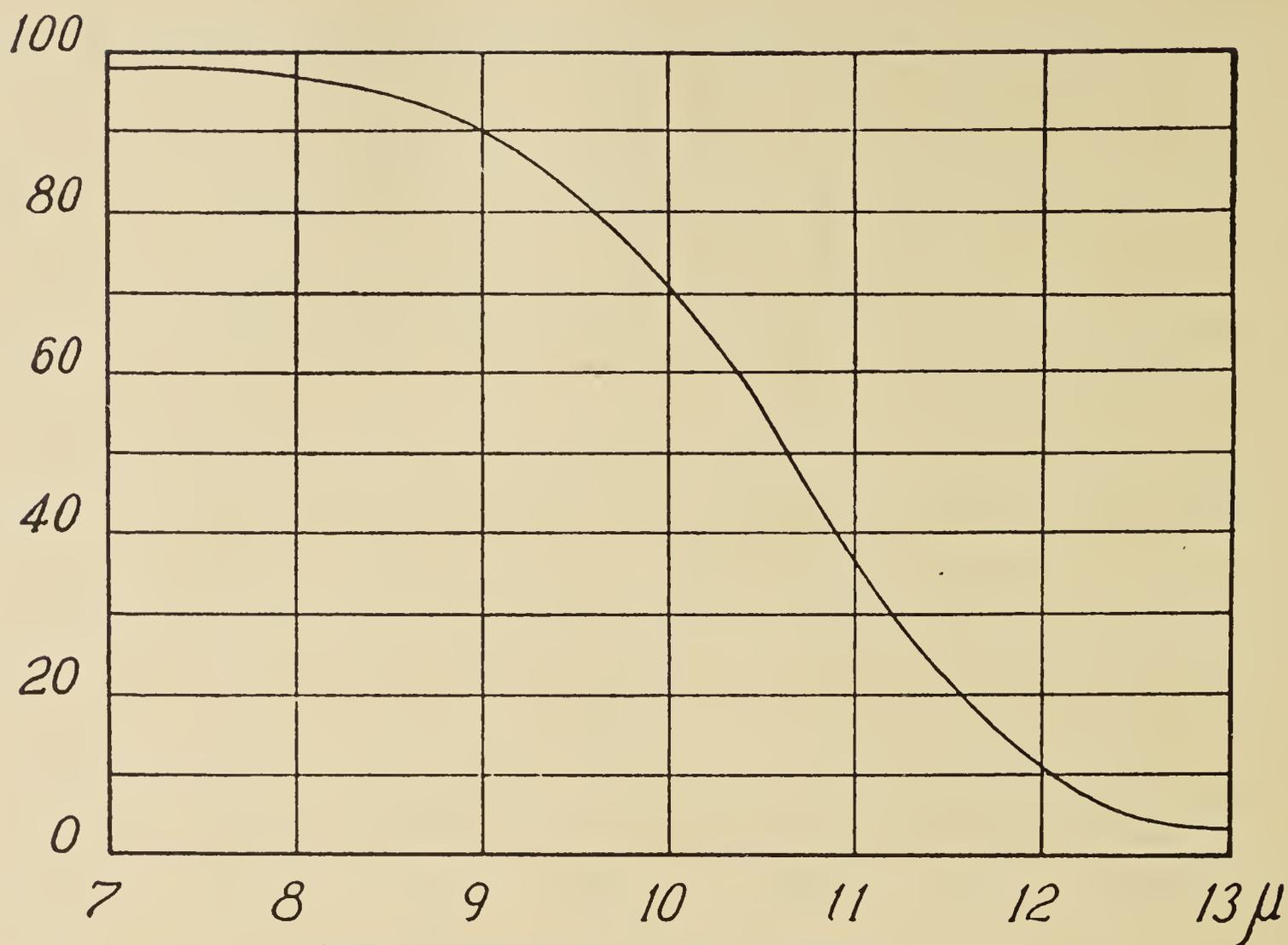


Figure 5. Transmission by fluorite; thickness 1 mm.

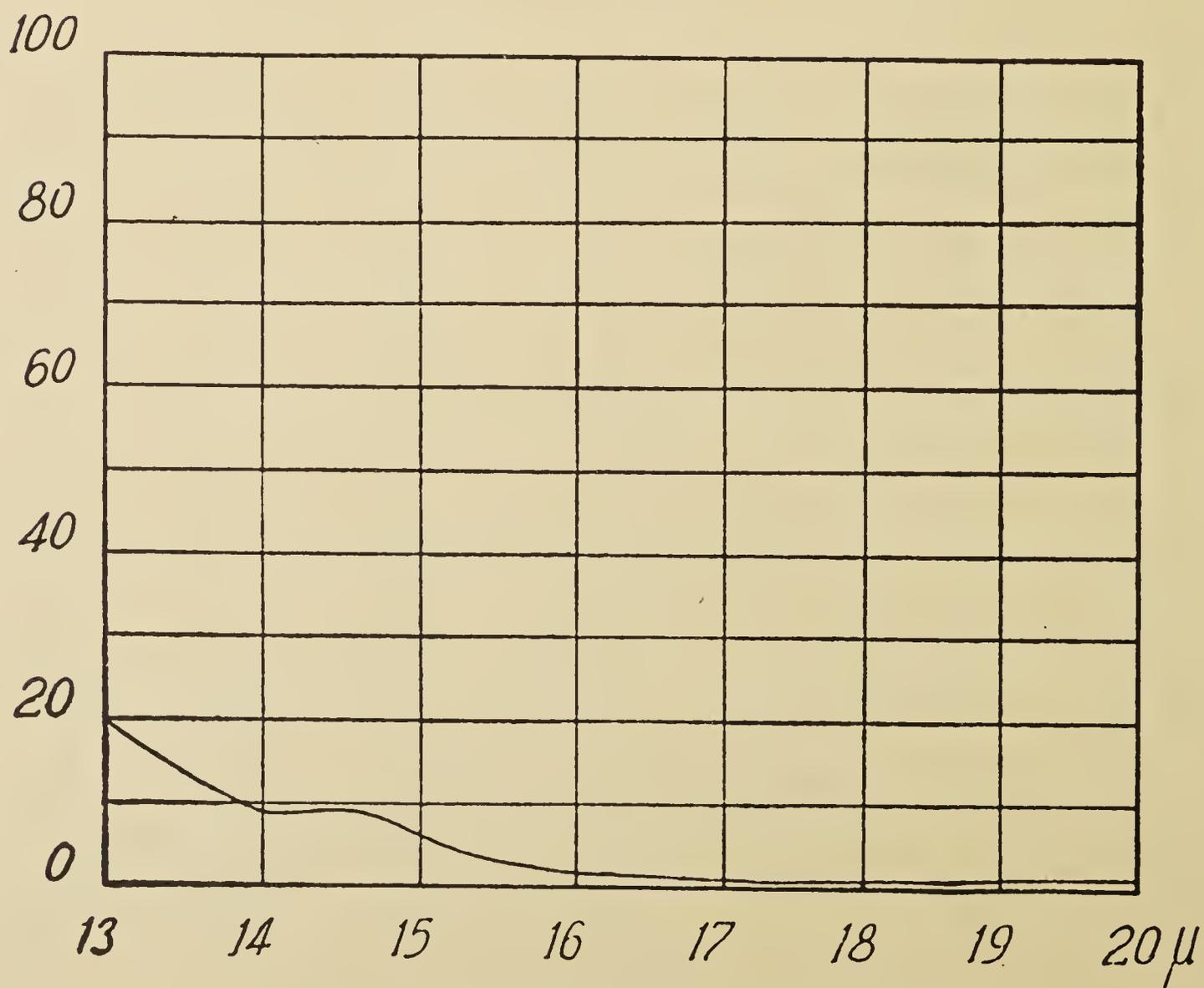


Figure 6. Transmission by fluorite; thickness 0.38 mm.

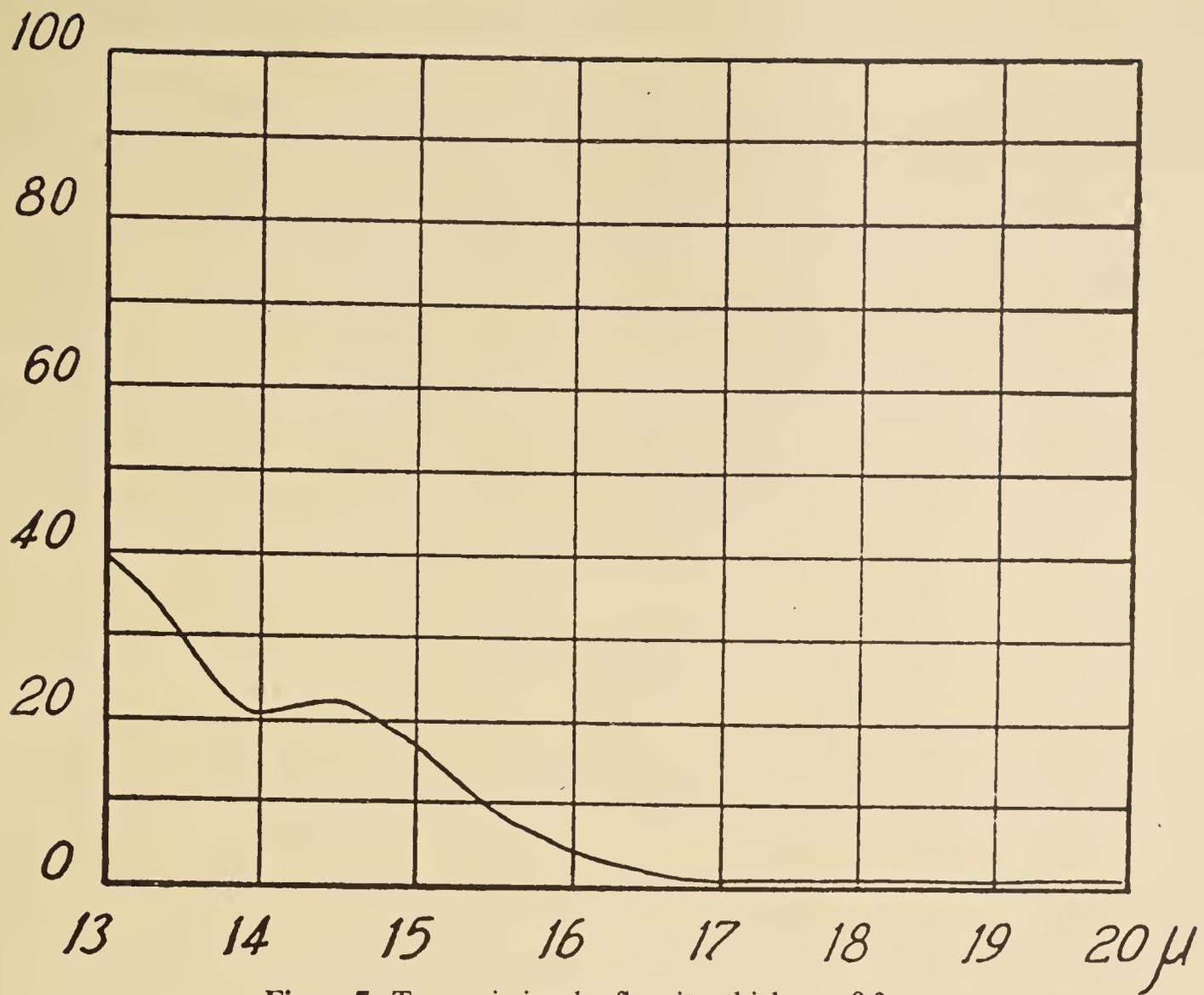


Figure 7. Transmission by fluorite; thickness 0.3 mm.

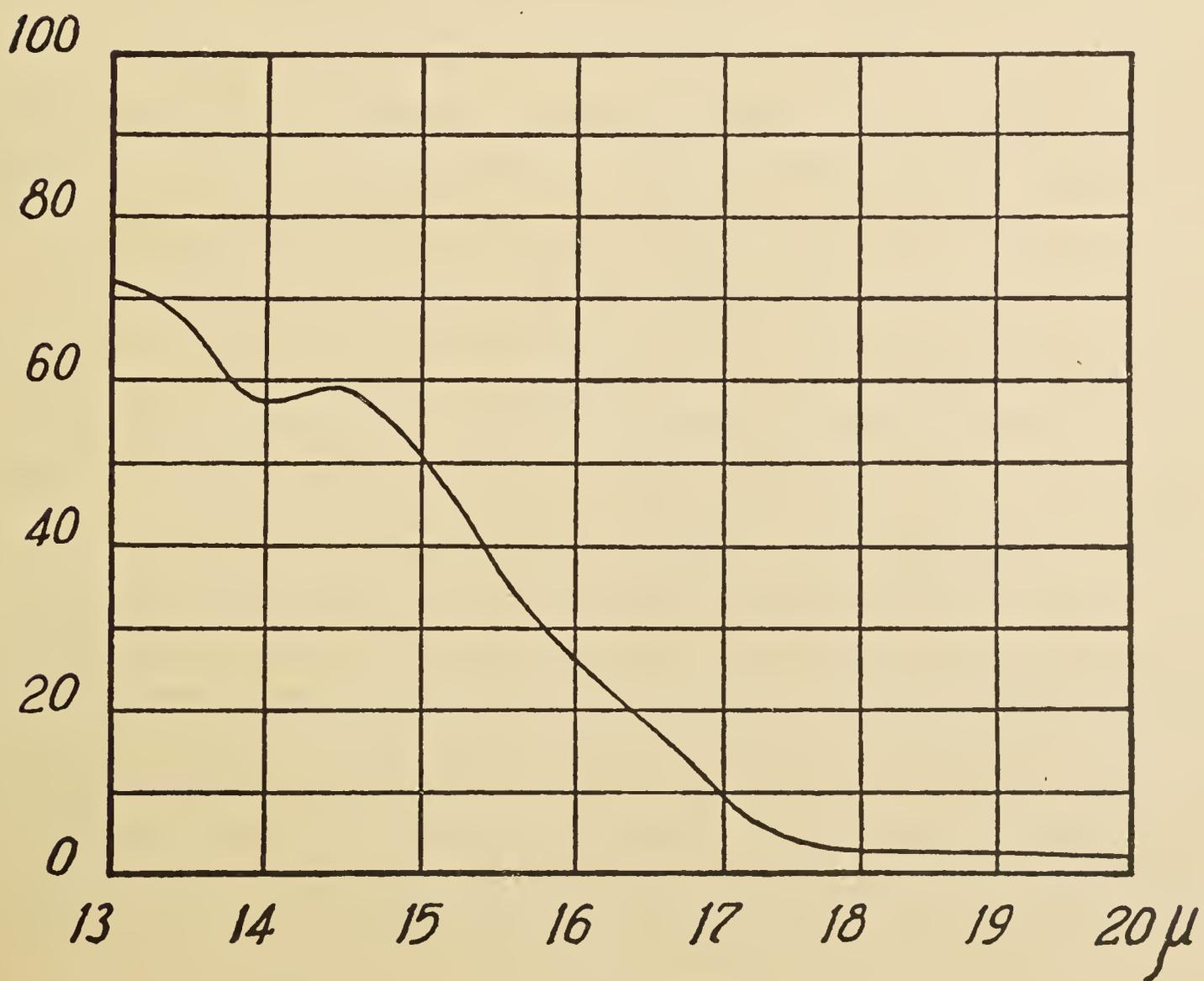


Figure 8. Transmission by fluorite; thickness 0.11 mm.

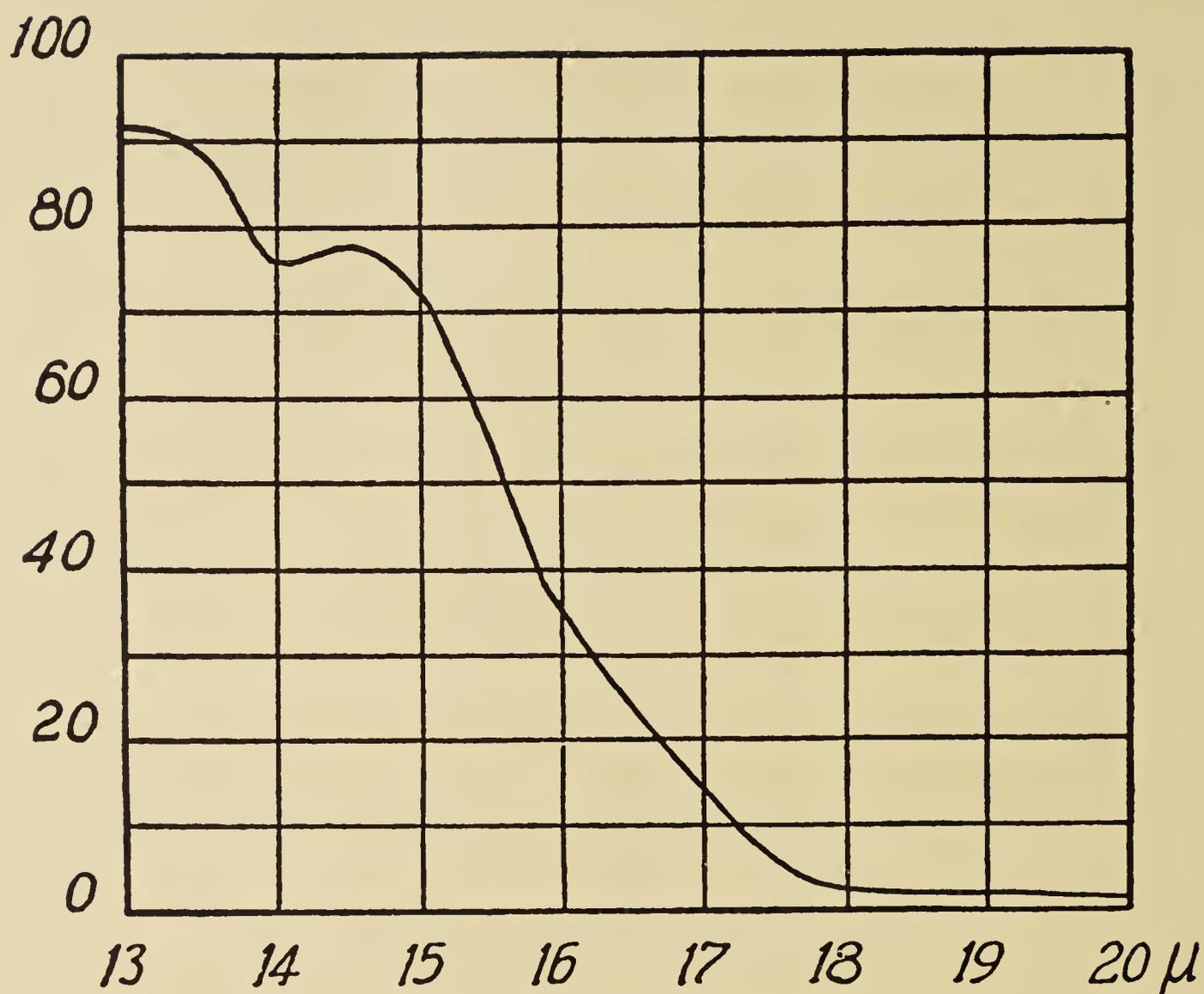


Figure 9. Transmission by fluorite; thickness 0.09 mm.

as a fundamental but as a series of overtones. Taking $28\ \mu$ as the characteristic infra-red wavelength and hence $357\ \text{cm}^{-1}$ as the frequency of that oscillation expressed as a wave-number, the octave of the fundamental would manifest itself in the absorption spectrum at $14\ \mu$, the third harmonic at $9.3\ \mu$ and the fourth harmonic at $7\ \mu$, these absorptions rapidly decreasing in strength. The appearance of absorptions of very different orders of magnitude at and near these wavelengths evident from the spectrophotometer records is thus satisfactorily explained. We accordingly recognise $28\ \mu$ as the wavelength corresponding to the fundamental mode of vibration referred to above and the dip at $14\ \mu$ in the transmission curve as due to the octave of that mode.

The appearance of a turning point or inflexion in the transmission curve at $15.6\ \mu$ is also readily explained. Expressed as a wave-number, the spectral frequency corresponding to that wavelength is $641\ \text{cm}^{-1}$ which is just double the frequency shift of $321\ \text{cm}^{-1}$ recorded as a sharply defined line in the scattering of monochromatic light by fluorite. This shift was first noticed by Rasetti who used the intense resonance radiation of a water-cooled and magnet-controlled mercury arc in his experiments. It has been confirmed using the same technique and excellent spectrograms showing the frequency shifts $\pm 321\ \text{cm}^{-1}$ have been obtained at this Institute. They are clearly ascribable to the second principal

mode of vibration of the fluorite structure in which the two lattices of fluorine atoms oscillate against each other in opposite phases. Considered as an independent normal mode, this vibration should be totally inactive in the infra-red both as a fundamental and as its overtones. Its contiguity in frequency to the principal mode of wave-number of 357 cm^{-1} which is strongly active both as a fundamental and as overtones would, however, influence its behaviour noticeably. We may indeed expect the mode of wave-number 321 cm^{-1} to exhibit a kind of induced infra-red activity both as a fundamental and as its various overtones. The form of the transmission curve actually seen in figure 8 and figure 9 thus receives a satisfactory elucidation.

Summary

The spectrophotometer records enable us to determine $28\ \mu$ as the characteristic wavelength and 357 cm^{-1} as the characteristic wave-number of the infra-red active mode of oscillation of the calcium and fluorine atoms against each other in opposite phases. This mode is active also as its overtones, the octave in particular appearing as a conspicuous and well-defined dip at $14\ \mu$ in the transmission curve. By reason of its contiguity in frequency with the strongly active mode, the vibration of the two fluorine lattices against each other which gives rise to an observable frequency shift in the scattering of monochromatic light also displays an induced infra-red activity and is recorded in the transmission curve as a sharp inflexion located at $15.6\ \mu$. The corresponding wave-number 641 cm^{-1} is just double the frequency shift of 321 cm^{-1} observed in light-scattering.

Spectroscopic evaluation of the specific heats of potassium bromide

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1. Introduction

KBr occupies a position of considerable importance amongst the alkali halides, as it is the material of the dispersing prisms commonly used for the range of wavelengths in the infra-red spectrum lying beyond the reach of rock-salt prisms. NaCl optics carries us up to $15\ \mu$, while KBr optics covers the range between 13 and $24\ \mu$ satisfactorily. The lower limit of $13\ \mu$ is set by the fact that the dispersive power becomes too small at lesser wavelengths, while the upper limit of $24\ \mu$ is determined by the fact that the loss of energy by absorption in the material of the prism becomes much too large at greater wavelengths. As has been shown in part VIII of the author's memoir on the alkali halides (reference 1), the absorption due to the infra-red activity of the principal mode of highest frequency in their structures passes successively from the first to the second, third and higher orders as we move towards shorter wavelengths, the strength of such absorption becoming rapidly weaker with increase of order. Hence, by noting the stepwise diminution in absorption with diminishing wavelength, it is possible to make a reliable estimate of the characteristic wavelength corresponding to the highest frequency of vibration of the structure.

Figure 1 shows the transmission percentages in the region of wavelengths between 17 and $24\ \mu$ of a rectangular block of KBr of the highest purity supplied by the firm of Karl Korth of Kiel, West Germany. The block was 40 mm long and 20 mm wide, and the two curves in the figure refer respectively to these two thicknesses. It will be noticed that the absorption is extremely weak at $17\ \mu$ and remains weak at $20\ \mu$, while beyond $21\ \mu$ it increases rapidly. The graphs thus indicate that the absorptions effective at 17 and $21\ \mu$ are of different orders of magnitude. If we assume that the absorption effective at $21\ \mu$ is of the fourth order, the characteristic wavelength of KBr comes out as $84\ \mu$ and its characteristic frequency expressed in wave-numbers as $119\ \text{cm}^{-1}$. The reliability of this procedure is confirmed by the fact that in the case of NaCl, a similar study of the spectrophotometric records enables us correctly to locate the wavelengths corresponding to the successive orders of absorption (reference 2).

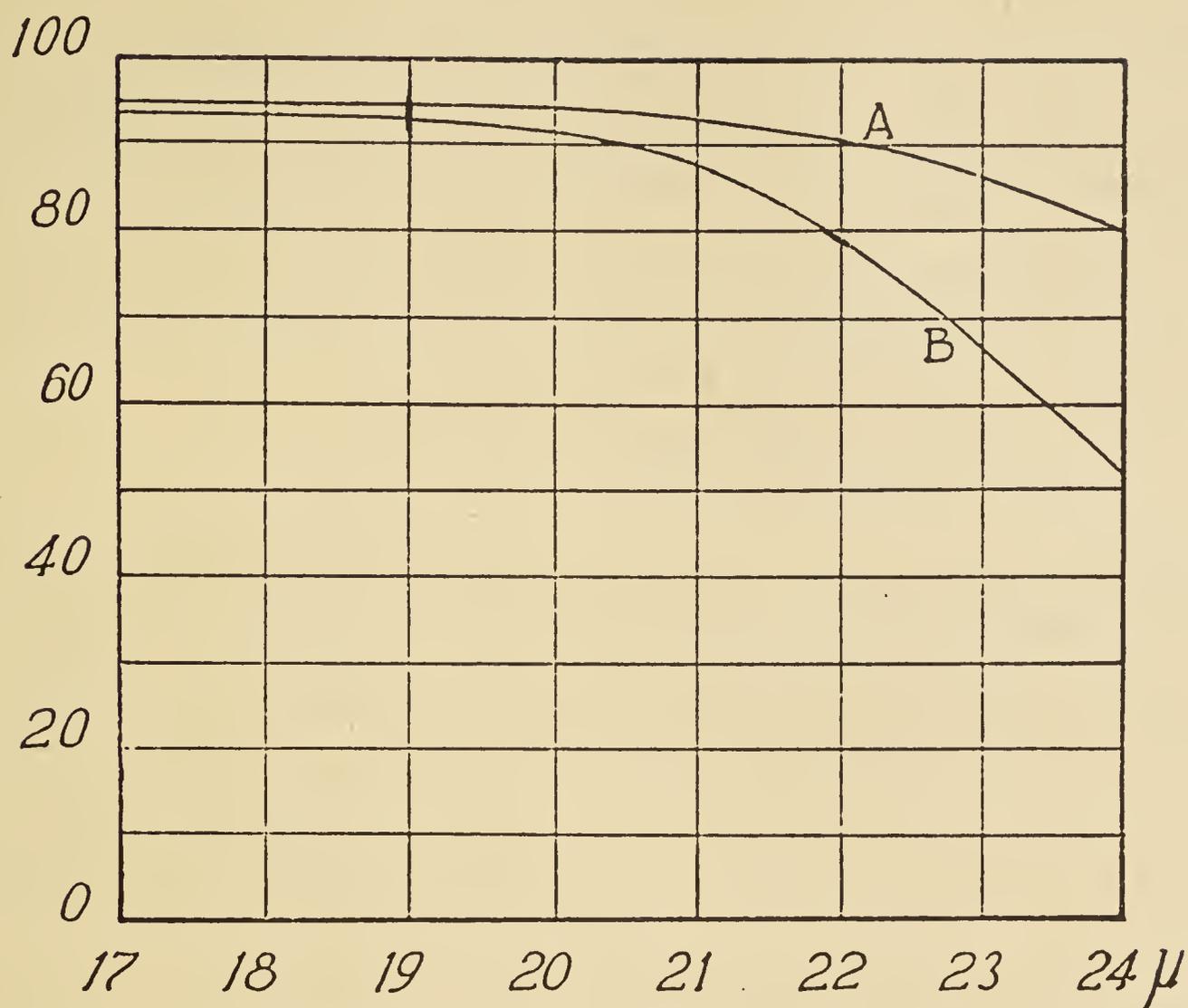


Figure 1. Infra-red transmission percentages of potassium bromide, (A) 20 mm path, (B) 40 mm path.

2. The spectrum of free vibrations

It is unnecessary here to traverse in detail, the derivation of the modes of free vibration of the structure of the alkali halides given in the memoir already quoted (reference 1). We shall therefore merely list the nine modes with their respective degeneracies as below.

Table 1 shows the four modes of coupled oscillation of the cubic layers arranged in diminishing order of frequency as indicated by the dynamical theory. The four modes of oscillation of the octahedral layers have like-wise been shown in the table arranged in the descending order of frequency amongst themselves. Obviously, however, it would be very helpful to arrange all the nine modes in a consolidated list in descending order of frequency. Part VI of the memoir already cited (reference 1) contains the theoretical considerations and numerical computations which enable this to be done. We reproduce here the computed frequencies of the nine modes arranged in descending order of frequency.

The degeneracies listed in table 2 and the description of the modes given in table 1 enable us to identify them individually. It has to be emphasised that the

Table 1

	Degeneracy
I. Oscillation of the potassium and bromine atoms in opposite phases	3
II. Coupled oscillations of the potassium and bromine atoms in the cubic planes:	
(a) Tangential to the planes in opposite phases	6
(b) Normal to the planes in the same phase	3
(c) Normal to the planes in opposite phases	3
(d) Tangential to the planes in the same phase	6
III. Oscillations of the atoms appearing in the octahedral layers:	
(a) Potassium atoms normal to the planes	4
(b) Potassium atoms tangential to the planes	8
(c) Bromine atoms normal to the planes	4
(d) Bromine atoms tangential to the planes	8
IV. Translations of all atoms in the same phase	3
Total	48

Table 2. KBr: Computed frequencies of free vibration (cm^{-1})

Degeneracy	3	6	3	4	8	4	8	3	6
Frequency	105	96	88	86	86	60	60	58	43

Table 3. KBr: Amended table of computed frequencies (cm^{-1})

Degeneracy	3	6	3	4	8	4	8	3	6
Frequency	119	108	99	97	97	68	68	66	49

computations of the frequencies as shown in table 2 do not claim any great accuracy. They have been made on the basis that only two force-constants α and β are taken into account and that those two force-constants are very simply related respectively to the bulk-modulus and to the rigidity modulus of the crystal. The neglect of all the force-constants except α and β results in making the frequencies of vibration having the degeneracies 4 and 8 which appear side by side in table 2 equal to each other, instead of the former being distinctly greater as is to be expected. In spite of these defects, the figures shown in table 2 serve as useful guides in the interpretation of the observed spectra. It has been remarked earlier

that the most strongly active mode of highest frequency has a frequency of 119 cm^{-1} as is indicated by the spectrophotometer records. In the light of this finding, we have to correct the frequencies listed in table 2. This may be done by increasing all the frequencies in the same proportion. The figures as thus amended are shown in table 3.

We shall presently see how the computed frequencies listed in table 3 can be made use of in the final evaluation of the spectroscopic data.

3. Activity of the modes

In part VIII of the memoir already cited (reference 1), the infra-red activities of all the nine normal modes of vibration have been discussed in detail. From the considerations there advanced, it emerges that when the electrical and mechanical anharmonicities of the vibrations are ignored, only the mode of vibration of the highest frequency can manifest itself in the absorption of infra-red radiation, while all the other eight modes are inactive. When, however, the finiteness of the amplitudes of vibration in the structural elements of the crystal is considered in conjunction with electrical anharmonicity, it emerges that the four coupled modes of vibration of the cubic layers of the crystal can be active in the absorptions of higher order, including especially that of the second-order in which they appear in the spectrum with doubled frequencies. The four modes of vibration of the octahedral layers, on the other hand, cannot exhibit such activity, for the movements involved are those of the potassium atoms only or of the bromine atoms only, normal to the layers in the modes of degeneracy 4 and tangential to them in the modes of degeneracy 8. The atomic layers of one species move symmetrically with respect to the layer of the other species of atoms located midway between them. Such symmetry results in cancelling out the electrical charge displacements even for finite amplitudes of vibration. Hence, provided the mechanical anharmonicity of the vibrations is ignored, the four octahedral modes would not display any activity as absorbers of infra-red radiation. The mechanical anharmonicity would result in certain modifications of these conclusions. These, however, do not concern us here.

In part IX of the memoir already cited (reference 1), the activity of the nine free modes of vibration of the alkali halides in the scattering of light with altered frequencies was discussed in considerable detail. It emerged that by reason of the symmetry properties of the structure, none of the nine modes can manifest itself as a frequency shift in the scattering of monochromatic light traversing the crystal. On the other hand, it was shown that all the nine modes could manifest themselves with *doubled* frequency, thus opening the way to the complete determination of the frequency spectrum from the spectrum of light scattering.

It is, however, important to remark that we cannot expect all the nine doubled frequency shifts corresponding to the different free modes of vibration to be

recorded with equal intensities in the spectrum of the scattered light. There are several considerations to be borne in mind in this connection. Firstly, we have to take note of the degeneracies of the respective modes. Apart from all other factors, the greater the degeneracy, in other words, the larger the number of distinct modes having the same frequency, the greater the intensity with which the modes would be recorded as a shift with doubled frequencies. In consequence, we may expect the two modes of degeneracy 8 to record themselves with notable intensities and the two modes of degeneracy 6 to follow them next in order, while the two modes of degeneracy 4 and the three modes of degeneracy 3 would have lesser intensities.

A second factor of importance in determining the strength with which particular frequency shifts would be recorded is the symmetry of the modes of vibration concerned. As has already been remarked, the four modes of vibration of the octahedral layers are of symmetric type, two layers of one atomic species moving in opposite phases and the intermediate layer of atoms of the other species remaining at rest. It is because of such symmetry that these modes do not display any infra-red activity even when the vibrations are of finite amplitude. It is well known that, in general, symmetric modes of vibration which do not exhibit infra-red activity are those which record themselves most strongly as frequency shifts in light-scattering and *per contra*, antisymmetric modes which exhibit strong infra-red activity fail to manifest themselves as frequency shifts in the light-scattering. On general grounds, therefore, we shall be justified in expecting that there would be a marked difference between the octahedral symmetric modes and the cubic antisymmetric modes in respect of their recorded intensities as doubled frequency shifts, the former being recorded more strongly than the latter.

Thirdly, we have also to consider the nature of the individual modes. Since we are concerned with the second-order scattering of double frequency, movements which involve a closer approach to each other of neighbouring atoms, in other words, involve a greater measure of optical inharmonicity, would give rise to greater intensity of light-scattering than the modes in which the approaches are less close. The two modes in which adjacent potassium and bromine atoms move together in the same phase and hence approach each other less closely would, therefore, manifest themselves more weakly than the two other modes in which they oscillate in opposite phases.

Finally, we have also to take note of the great difference in the refractivity of the two species of atoms with which we are concerned. The bromine atoms have a greater refractivity than the potassium atoms. Hence the two modes in which the former alone approach or recede from each other may be expected to record themselves as frequency shifts more strongly than the corresponding modes in which the potassium atoms alone oscillate with respect to each other.

We may sum up the foregoing remarks by the following statements. The observed frequency shifts would divide themselves into two groups differing in their intensities, the six having degeneracies of 8, 6 or 4 being of greater intensity

and the three others with degeneracy 3 of a smaller intensity. In the first group, the modes of degeneracy 8 would appear more strongly than those of degeneracy of 4, and amongst these again, the modes in which the bromine atoms alone oscillate would be recorded more strongly than those in which the potassium atoms alone oscillate. In the second group of riply degenerate oscillations, that having the lowest frequency would appear much more feebly than the other two.

4. The spectrum of light scattering

As has already been explained in part IX of the memoir already cited (reference 1), the fact that the frequency shifts in light scattering recorded with the alkali halides are only those of the second-order gives rise to special difficulties in experimentation. These can only be overcome by use of material of the highest quality and guarding against the several pitfalls which await the unwary experimenter. For this reason and the importance of obtaining complete data which could be absolutely relied upon, it appeared necessary to undertake a fresh and independent investigation at this Institute of the case of potassium bromide. This was made with the block of perfectly pure KBr supplied by Karl Korth mentioned earlier.

The well known technique was employed in which a water-cooled magnet-controlled mercury arc in quartz illuminates the crystal. A filter of mercury vapour put inside the spectrograph prevents the photographic plate being fogged by the intense resonance radiation entering the instrument. The crystal block was placed as close as possible to the quartz tube containing the arc, the latter being kept pressed against the side of the tube nearest the crystal by the action of the magnetic field. An excessive heating of the crystal was avoided by a current of air kept blowing on it throughout the exposure. To obtain a well-exposed picture with KBr, an exposure of eight hours was found to be necessary, using the medium-size quartz spectrograph.

It should be emphasised that the filter of mercury vapour inside the instrument cuts out only the core of the resonance radiation. In the spectrum recorded with an eight-hour exposure, the rest of the radiation emitted by the mercury vapour and entering the spectrograph in whatever fashion would necessarily appear. Its intensities would naturally be greatest in the spectral regions not far removed from the position of the resonance radiation. As a matter of actual experience, the resulting continuum appears more conspicuously in the region of greater wavelengths and therefore of lower frequencies than the resonance radiation. The failure to recognise the presence and actual origin of this continuum is one of the pitfalls awaiting the experimenter in this field. It should be noted that Rasetti who devised the technique employed fell into the same error and made the mistake of identifying the continuum as part of the effect under study by him in the case of rock-salt.

Since the frequency shifts in the cases of KBr are substantially smaller than in the case of NaCl, the overlap with the continuous radiation of the mercury arc might have had serious consequences. Fortunately, however, the refractive index of KBr is higher than that of NaCl and hence its scattering power is much greater. Thus, the presence of the continuous background does not actually interfere with the possibility of recognising the significant features in the recorded spectrum of KBr.

5. The recorded spectral shifts

The spectrum of KBr recorded with the arrangements described above and an eight-hour exposure is reproduced as figure 1 in plate I. The observed frequency shifts have been marked in figure 2 in plate II. Both positive and negative frequency shifts appear in the recorded spectra, thus affording a welcome confirmation of their reality and enabling them to be identified without any possibility of error. The spectrum of the arc is reproduced alongside that KBr in plate I for comparison with it. The continuum referred to above can be recognised in it.

A visual examination of the recorded spectrum shows three sharply defined lines which are clearly resolved from each other, their frequency shifts being respectively 122 , 142 and 169 cm^{-1} respectively. Of these, the first is the most intense and is accordingly identified as arising from the eight-fold degenerate oscillation of the bromine atoms. The second has likewise been identified as arising also from the oscillation of the bromine atoms with a degeneracy 4. The third line is ascribable to the eightfold degenerate oscillations of the potassium atoms.

The two other features which appear conspicuously in the spectrum as well-defined lines exhibit frequency shifts of 85 and 215 cm^{-1} respectively. The latter is clearly ascribable to the sixfold degenerate coupled oscillations of the potassium and bromine atoms in the cubic layers. The frequency shifts of $\pm 85\text{ cm}^{-1}$ are also sharp and clear, the positive shift which is less disturbed by the overlapping continuum being especially sharp and clear. This is recognized as the mode of oscillation with degeneracy 6 having the lowest frequency. The shift of 240 cm^{-1} recorded in the spectrum is distinctly diffuse and therefore rather weak. It has been identified as the mode of oscillation with degeneracy three and having the highest frequency. Adjacent to the frequency shift of 215 cm^{-1} appears a diffuse band which is clearly a superposition of two frequency shifts. These have been identified as due to the oscillation of degeneracy 4 with a frequency shift of 196 cm^{-1} and an oscillation of degeneracy 3 with a frequency shift of 184 cm^{-1} .

Finally, between the sharply defined lines at 85 cm^{-1} and 122 cm^{-1} , there appears a weak line recorded with frequency shifts of $\pm 140\text{ cm}^{-1}$. This has been

identified as the triply degenerate oscillation of the potassium and bromine in the cubic layers.

All these features can also be recognized in the reproduced spectra. They have been entered below in table 4.

Table 4. Observed frequency shifts and their identification (cm^{-1})

Degeneracy	3	6	3	4	8	4	8	3	6
Observed shifts	240	215	184	196	169	142	122	104	85
Halved values	120	108	92	98	85	71	61	52	42
Computed values (table 3)	119	108	99	97	97	68	68	66	49

6. Computation of the specific heats

It will be seen from table 4 that there is a satisfactory general agreement between the spectroscopically determined frequencies and those dynamically computed a priori and shown in table 3. The identifications of the spectroscopically determined frequencies with the different modes of known degeneracies have not been arbitrarily made, but are based on considerations of both frequency and intensity as set out earlier. We can, therefore, confidently proceed to an evaluation of the specific heats of KBr as a function of the temperature on the basis of the spectroscopically determined frequencies.

Table 5 shows the details of the computation which follows the same lines as those adopted in numerous cases in the later chapters of the memoir already cited (reference 1). It is, therefore, unnecessary to explain the procedure here in detail. A comparison between the observed and computed specific heats is made at the foot of table 5. The general trend of the temperature dependence of the specific heat is clearly indicated by the theoretical computations. Quantitatively, however, the agreement can by no means be considered satisfactory. The reason for this is not far to seek. In the actual recording of the spectrum of the light scattered by the crystal, the latter was distinctly warmed up by the heat emanating from the mercury arc and its temperature was about 350°K . On the other hand, the experimentally determined specific heats cover the temperature range between 10 and 200°K , the most rapid variation being in the temperature range 20 and 60°K . Hence, to obtain a satisfactory representation of the specific heat data on the basis of the spectroscopically determined frequencies, the latter should have been recorded with the crystal held at about 40°K instead of at 350°K as was actually the case. It can by no means be supposed that the spectrum of free vibrations of the lattice would remain unaltered as between such widely different temperatures.

Table 5. Comparison of the computed and observed values of the atomic heats of potassium bromide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
3E(120)	—	0.0004	0.0045	0.0918	0.1913	0.2534	0.2903	0.3324	0.3491
6E(108)	—	0.0023	0.0175	0.2339	0.4312	0.5443	0.6073	0.6805	0.7071
4E(98)	0.0001	0.0033	0.0200	0.1887	0.3161	0.3827	0.4198	0.4606	0.4761
3E(92)	0.0001	0.0039	0.0205	0.1567	0.2491	0.2958	0.3213	0.3486	0.3587
8E(85)	0.0006	0.0174	0.0777	0.4713	0.7031	0.8158	0.8738	0.9377	0.9616
4E(71)	0.0017	0.0237	0.0758	0.2920	0.3891	0.4330	0.4544	0.4772	0.4854
8E(61)	0.0108	0.0934	0.2353	0.6689	0.8299	0.8964	0.9297	0.9646	0.9770
3E(52)	0.0108	0.0613	0.1265	0.2780	0.3265	0.3455	0.3549	0.3644	0.3680
6E(43)	0.0556	0.2053	0.3472	0.6088	0.6805	0.7080	0.7204	0.7339	0.7398
3D(43)	0.0905	0.1775	0.2381	0.3302	0.3525	0.3612	0.3650	0.3690	0.3705
Calculated C_v	0.1702	0.5885	1.1613	3.3203	4.4693	5.0361	5.3369	5.6689	5.7933
Experimental C_v	0.116	0.390	0.802	2.650	3.934	4.663	5.076	5.572	5.771

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc. (Lond.)* **A242**, 471 (1957).

Table 6 shows a fresh computation of the specific heats of potassium bromide in which all the observed spectral frequencies have been increased uniformly by 10 per cent of their values. An increase of this magnitude is justifiable in view of what is known regarding the temperature changes of the low-lying lattice frequencies of various crystals, such as calcite and quartz, which have been determined by studies on light-scattering with the crystals held at liquid air and at room temperatures respectively. The increase of 10 per cent made also appears fully justified in view of our knowledge of the great increases in the elastic constants of the alkali halides and especially of their bulk moduli which occur when they are cooled down to very low temperatures.

Table 6. Comparison of the computed and observed values of the atomic heats of potassium bromide

	10° K	15° K	20° K	40° K	60° K	80° K	100° K	150° K	200° K
3E(132)	—	0.0002	0.0023	0.0713	0.1681	0.2345	0.2755	0.3253	0.3449
6E(119)	—	0.0009	0.0095	0.1879	0.3875	0.5103	0.5821	0.6662	0.6993
4E(108)	—	0.0015	0.0117	0.1560	0.2874	0.3629	0.4049	0.4537	0.4714
3E(101)	—	0.0019	0.0128	0.1339	0.2301	0.2830	0.3119	0.3439	0.3558
8E(94)	0.0002	0.0089	0.0491	0.4040	0.6530	0.7825	0.8512	0.9269	0.9544
4E(78)	0.0007	0.0144	0.0547	0.2639	0.3707	0.4208	0.4462	0.4732	0.4832
8E(67)	0.0053	0.0623	0.1813	0.6183	0.7994	0.8770	0.9170	0.9585	0.9733
3E(57)	0.0063	0.0453	0.1038	0.2628	0.3178	0.3408	0.3516	0.3630	0.3669
6E(47)	0.0368	0.1645	0.3030	0.5869	0.6693	0.7003	0.7158	0.7316	0.7382
3D(47)	0.0744	0.1575	0.2204	0.3231	0.3491	0.3588	0.3636	0.3683	0.3701
Calculated C_v	0.1237	0.4574	0.9486	3.0081	4.2324	4.8709	5.2198	5.6106	5.7575
Experimental C_v	0.116	0.390	0.802	2.650	3.934	4.663	5.076	5.572	5.771

Experimental values from Berg, W T and Morrison, J A, *Proc. R. Soc. (Lond.)* **A242**, 471 (1957).

A satisfactory agreement between the computed and observed values of specific heat emerges from the figures shown at foot of table 6. There is thus little doubt that the discrepancies noticed in table 5 have the origin indicated above.

Summary

The spectrum of free vibrations of the structure of potassium bromide is determined spectroscopically from the scattering within the crystal of the resonance radiation of the mercury arc. The modes are recorded with doubled frequency shifts. The identification of these shifts as arising from the various modes of vibration is made on the basis of the frequencies as computed a priori from the dynamic theory and from a consideration of their observed spectral intensities. From these spectral frequencies, the specific heat of the crystal can be evaluated as a function of the temperature. When the variations with temperature of the vibration frequencies are taken into account, a satisfactory agreement emerges between the theoretically computed and experimentally observed specific heat data.

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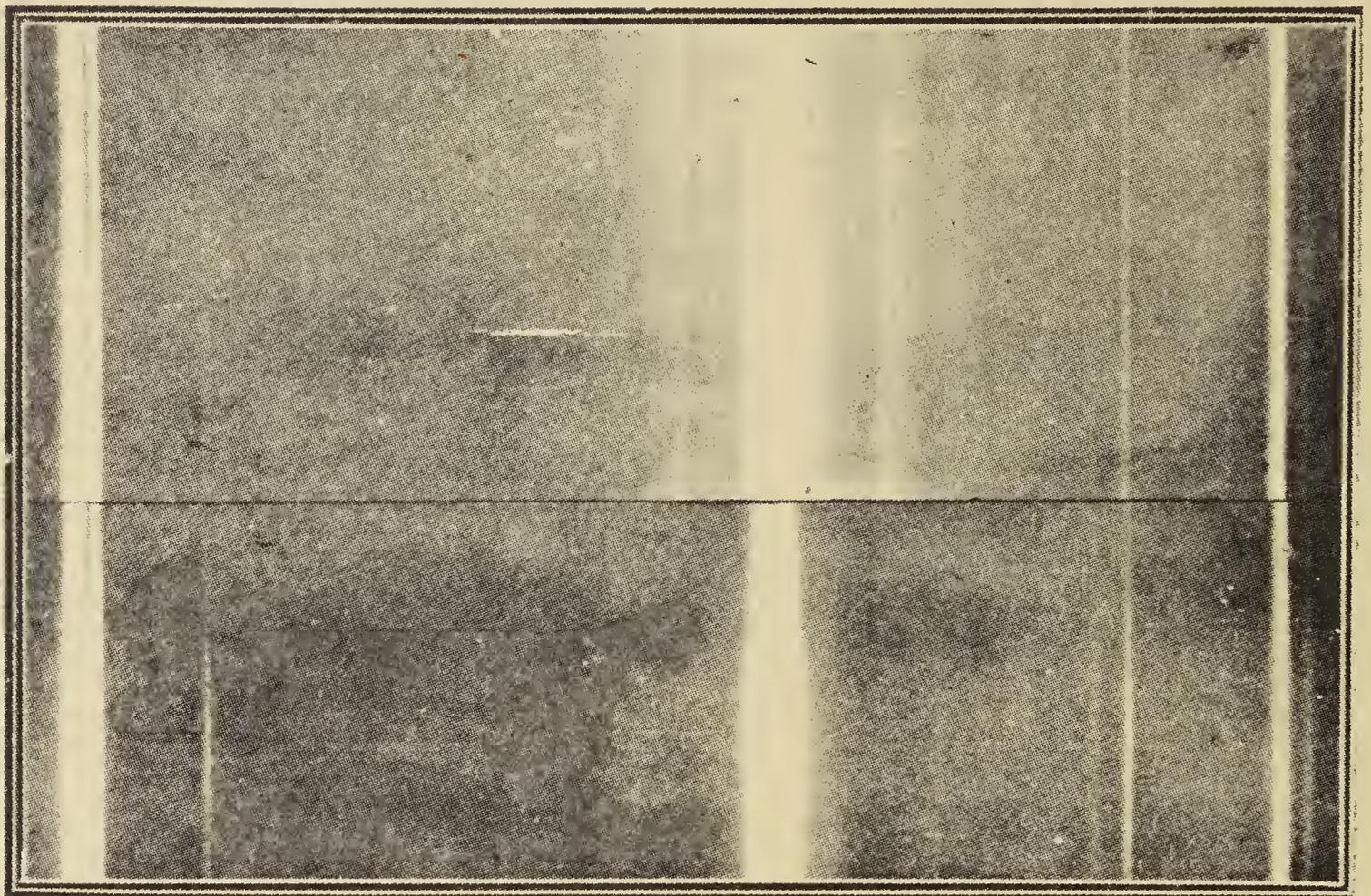


Figure 1. KBr: Frequency shifts in light scattering.

Plate I

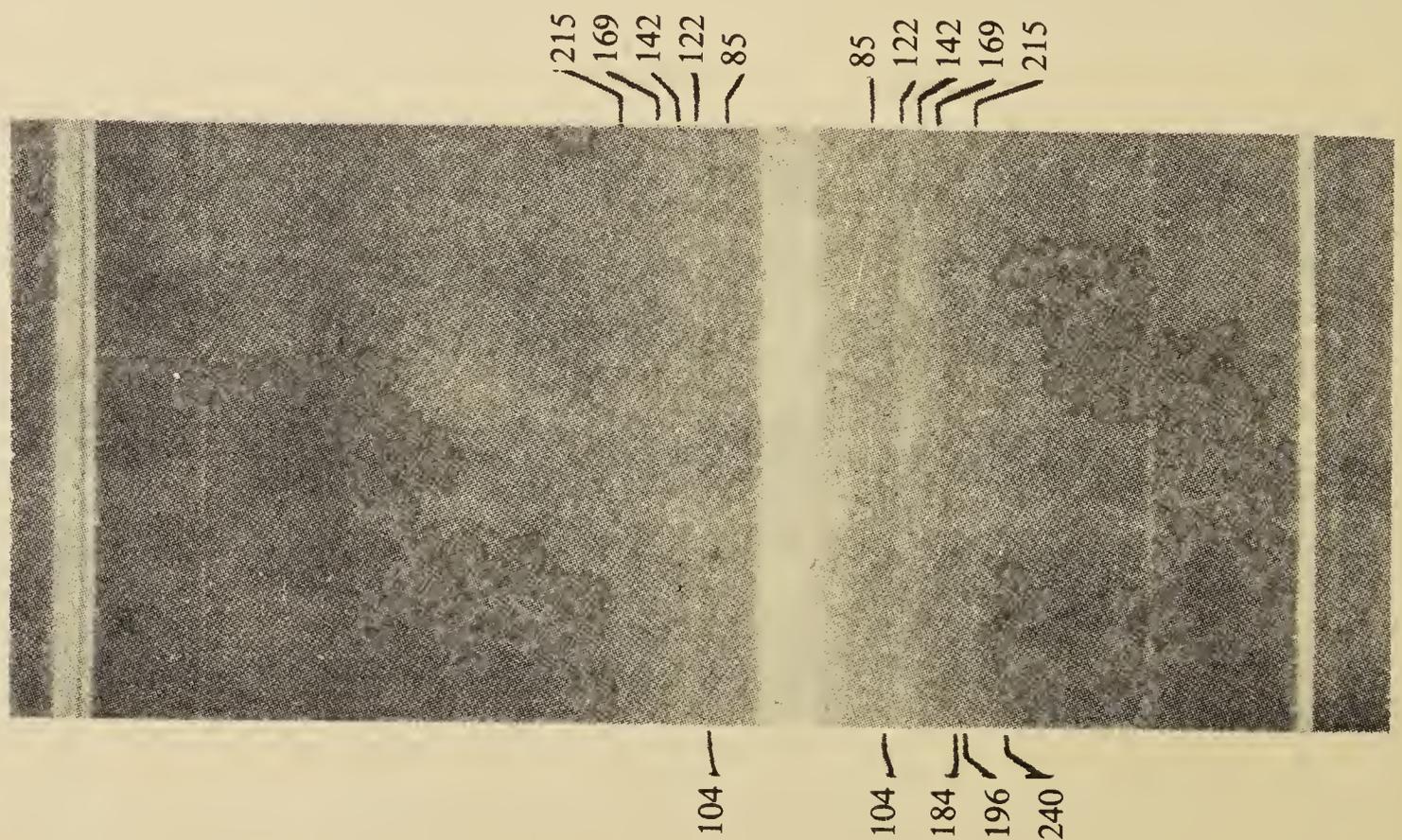


Figure 2. KBr: Frequency shifts in light scattering.

Plate II

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 232. CENTENARY OF THE FARADAY EFFECT [1945 *Curr. Sci.* **14** 281]
 233. SCIENCE IN EASTERN EUROPE: I [1958 *Curr. Sci.* **27** 371]
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 235. ZONAL WINDS AND JET STREAMS IN THE ATMOSPHERE [1967 *Curr. Sci.* **36** 593]
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 240. ON IRIDESCENT SHELLS—PART III. BODY-COLOURS AND DIFFUSION-HALOES [1934 *Proc. Indian Acad. Sci.* **A1** 859]
 241. THE STRUCTURE AND OPTICAL BEHAVIOUR OF IRIDESCENT SHELLS [1954 *Proc. Indian Acad. Sci.* **A39** 1; with D Krishnamurti]
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1. Diffuse X-ray Reflections

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293. REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY PART I. THEORETICAL DISCUSSION [1940 *Proc. Indian Acad. Sci.* A11 379; with P Nilakantan]
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295. REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY PART III. THE CASE OF SODIUM NITRATE [1940 *Proc. Indian Acad. Sci.* A11 398; with P Nilakantan]
296. QUANTUM THEORY OF X-RAY REFLECTION AND SCATTERING PART I. GEOMETRIC RELATIONS [1940 *Proc. Indian Acad. Sci.* A12 83; with N S Nagendra Nath]
297. REFLECTION OF X-RAYS WITH CHANGE OF FREQUENCY PART IV. ROCK SALT [1940 *Proc. Indian Acad. Sci.* A12 141; with P Nilakantan]
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300. THE QUANTUM THEORY OF X-RAY REFLECTION: BASIC IDEAS [1941 *Proc. Indian Acad. Sci.* A14 317]
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307. NEW PATHS IN CRYSTAL PHYSICS [1947 *Curr. Sci.* **16** 67]
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317. THE VIBRATION SPECTRA OF CRYSTALS AND THE THEORY OF THEIR SPECIFIC HEATS [1951 *Proc. Indian Acad. Sci.* **A34** 141]

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319. THE ELASTIC BEHAVIOUR OF ISOTROPIC SOLIDS [1955 *Proc. Indian Acad. Sci.* **A42** 1; with K S Viswanathan]
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321. EVALUATION OF THE FOUR ELASTIC CONSTANTS OF SOME CUBIC CRYSTALS [1955 *Proc. Indian Acad. Sci.* **A42** 111; with D Krishnamurti]

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322. THE NATURE OF THE THERMAL AGITATION IN CRYSTALS [1955 *Proc. Indian Acad. Sci.* **A42** 163]
323. THE THERMAL ENERGY OF CRYSTALS [1955 *Curr. Sci.* **24** 357]
324. QUANTUM THEORY AND CRYSTAL PHYSICS [1956 *Curr. Sci.* **25** 377]

325. THE PHYSICS OF CRYSTALS [1956 *Proc. Indian Acad. Sci.* **A43** 327]
326. THE SPECIFIC HEATS OF CRYSTALS: PART I. GENERAL THEORY [1956 *Proc. Indian Acad. Sci.* **A44** 153]
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