

# THE PHYSICS OF CRYSTALS\*

BY SIR C. V. RAMAN

(Memoir No. 85 of the Raman Research Institute, Bangalore 6)

Received May 31, 1956

## 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 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

---

\* Address to a Conference of Nobel Laureates at Lindau on the Lake of Constance, June 25th to 29th, 1956.

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 lacunæ 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 monatomic 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 cases 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 doubled 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.