The vibration spectrum of a crystal lattice

SIR C V RAMAN

Department of Physics, Indian Institute of Science, Bangalore

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 nucleii 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

$$\tfrac{1}{2}m_p[\dot{q}_{x\rho\sigma}^2 + \dot{q}_{y\rho\sigma}^2 + \dot{q}_{z\rho\sigma}^2]. \tag{1}$$

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

$$\tfrac{1}{2}K_{xrs}^{y\rho\sigma} \cdot q_{xrs} \cdot q_{y\rho\sigma} \tag{2}$$

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

$$K_{xrs}^{y\rho\sigma} = K_{y\rho\sigma}^{xrs}. \tag{3}$$

Hence, since each distinct pair of co-ordinates appears twice over in the summation, we may replace the factor $\tfrac{1}{2}$ by 1 in (2), it being understood that they are written together only once. The factor $\tfrac{1}{2}$ 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

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

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

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

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 rth 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

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

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

$$K_{xrs}^{xrs} = K_{xrs'}^{xrs'}, \tag{7}$$

$$K_{xrs}^{y\rho\sigma} = K_{xrs'}^{y\rho\sigma'}, \tag{8}$$

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

$$\frac{q_{xrs}}{q_{xrs'}} = \frac{q_{y\rho\sigma}}{q_{y\rho\sigma'}}, \tag{9}$$

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 is 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

$$\frac{q_{y\rho\sigma}}{q_{xrs}} = \frac{q_{y\rho\sigma'}}{q_{xrs'}}. \tag{10}$$

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

$$\alpha = \pm 1, \quad \beta = \pm 1, \quad \gamma = \pm 1. \tag{11}$$

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

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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 unmistakeable 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

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*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 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.,

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

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 o 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

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

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 o or π, the

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[†]*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 $1332 \, \text{cm}^{-1}$ 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 $1332 \, \text{cm}^{-1}$ 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

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*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.