

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 wave-lengths 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 wave-lengths 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

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

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

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

or of the form

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

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 $(24p - 3)$ eigen-vibrations 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

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

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 "wave-length" 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 $N_1N_2N_3$.

Equation (7) connects the "wave-length" 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

$$N = N_1N_2N_3 \quad (8)$$

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 wave-length λ of the vibration with the reciprocals of certain spacings d_1, d_2, d_3 whose product $d_1d_2d_3$ is equal to the volume of the super-lattice cell. As N_1, N_2, N_3 are very large numbers, the wave-lengths 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 wave-lengths ” 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 wave-lengths 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 wave-lengths of the elastic eigenvibrations are so chosen as to satisfy these relations, 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 wave-lengths provided by (9) to an enumeration on a scale of frequencies, we must, of course, take account of the fact that the ratio of wave-length 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 Fig. 1. A similar figure with the arrows parallel to the atomic

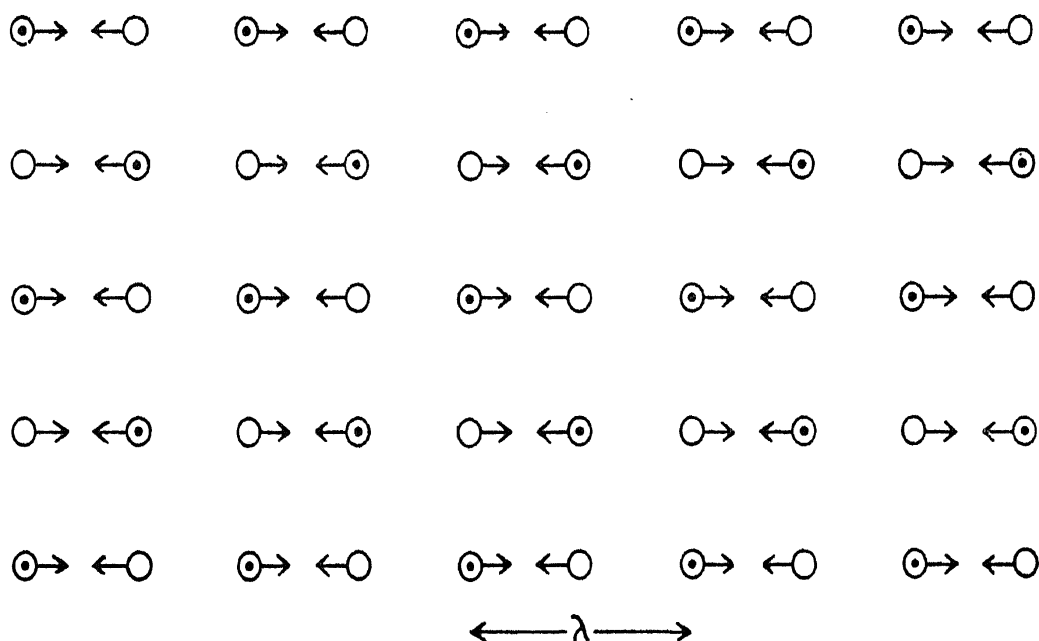


FIG. 1. Eigenvibrations of a Face-centred Cubic Lattice

planes would represent the tangential 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 "wave-length" which as seen from the figure is *twice* the distance between the atomic layers. Fig. 2 represents an elastic vibration properly so-called with the smallest possible wave-length; every alternate layer of atoms is a nodal plane which remains at rest, while the intervening planes of atoms move in opposite phases. The "wave-length" 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 wave-length.



FIG. 2. Elastic Vibrations of Minimum Wave-length in a Face-centred Cubic Lattice

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 "wave-lengths" 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 wave-lengths is however altogether different from that contemplated by equation (9) above in which they form a densely crowded sequence

with wave-lengths 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 wave-length at four times the lattice spacings, we must for all larger wave-lengths 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 wave-lengths superposed on each other. All the three possible kinds of elastic vibration are assumed to have frequencies inversely proportional to their respective wave-lengths 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 wave-length 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 wave-lengths would be one-half of those derived in the present paper. The additional eigenvibrations are those having the smallest wave-lengths 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. Figs. 1 and 2 above show respectively the characteristic eigenvibrations of the structure and the elastic vibrations of minimum wave-length 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 "wave-lengths" 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 Figs. 1 and 2, but there is clearly no possibility of a stationary vibration with these characters and of wave-length intermediate between twice and four times the atomic spacing. We can, of course, postulate waves of any intermediate wave-length 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 wave-lengths, each set corresponding to a group of wave-lengths 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 wave-lengths, 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 "wave-lengths" 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 wave-lengths when these are small, and hence the assumed distribution of wave-lengths 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 wave-lengths 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 wave-lengths 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.

6. 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 wave-lengths 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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