

New paths in crystal physics

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

The atomic vibration spectrum

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

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

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

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

Remarks on some earlier theories

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

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

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

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

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

Experimental configuration of the new ideas

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

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

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

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