THE FUNDAMENTALS OF CRYSTAL PHYSICS*

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THE crystal is Nature's most highly finished product in the field of atomic architecture. The majority of solids we handle in our daily lives are crystals by virtue of their structure, and their behaviour is largely determined by the properties of the crystalline state of matter. The fundamental aspects of crystal physics may, therefore, be of interest to many who are not professional physicists and I feel justified in making them the subject of my address to-day. I will leave it to my friend and colleague, Dr. Birbal Sahni, to voice the appreciation by our Fellows of the kindness and hospitality of our Hyderabad friends which has made our meeting here together in these difficult days possible.

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As is well known, the study of the beautiful external forms exhibited by well-developed crystals enables them to be grouped into classes exhibiting specific types of geometric symmetry. One of the most firmly established results of crystal physics is the existence of fundamental relationships between these symmetry classes and the various physical properties which the crystals belonging to them exhibit. Indeed, if the symmetry of the crystal is known, the branch of mathematical analysis known as group theory enables us to predict the general nature of its behaviour in respect of any specified physical property. By way of illustration, I may refer to a recent paper by Principal Bhagavantam in our *Proceedings*, in which he has discussed the elastic, optical and elasto-cptic properties of different crystal classes and corrected the results obtained earlier by Pockels. The existence of such relationships is a natural consequence of the fact that a crystal is essentially an ordered arrangement of the ultimate particles of matter in a regular geometric pattern. . Crystal architecture is based on the space-lattices which are formed by three sets of parallel and equidistant planes in space intersecting each other at a set of points which form a three-dimensional net or repetitive pattern. Each point of the lattice is occupied by an atom of the same kind, and all the atoms in the lattice are, therefore, equivalent. The simplest crystals consist of a single space-lattice and contain only one species of atom. More complicated crystals contain two, three or more sets of equivalent atoms, the space-lattices occupied by the different sets being geometrically similar and similarly situated, but not coincident. In other words, a crystal contains as many similar interpenetrating space-lattices as there are sets of equivalent atoms in it.

It is obvious, however, that a purely static conception of crystal architecture is inadequate. We must consider also the possible movements of the atoms away from the lattice points at which, on the average, they are placed. The importance of ascertaining and describing the atomic movements cannot be overemphasised. The thermal energy in a crystal is essentially the mechanical energy of such movements, and the thermal agitation of the atoms determines or modifies practically every observable property of the solid. Further, the amplitudes and frequencies of the possible atomic vibrations are determined by the forces which hold the atoms together in the form of a coherent solid. Hence, a knowledge of the atomic vibration spectrum of the crystal is essential for an understanding of its ultimate structure and indeed also of all the properties characteristic of the solid state. It is, therefore, necessary to find an answer to the question, what are the modes and frequencies of the possible vibrations of the atoms in a crystal about their positions of equilibrium in the space-lattice?

There are two ways in which an answer has been sought to this question. One way is to take the well-known theory of the vibrations of an elastic solid as the starting point and extrapolate it to the very limit. For this purpose, it is assumed that the atomic vibrations which occur on an extremely minute scale and as rapidly as a hundred or a thousand million times per second are determined by the same principles and considerations as are the visible and audible vibrations of a bell or a tuning-fork. It may be questioned whether such an extrapolation from macroscopic to molecular physics is theoretically justifiable. The other approach to the problem is the atomistic one. We fix our attention on the individual atoms located at the points of the space-lattice and ascertain the forces which come into play when they are displaced from these positions and calculate the resulting movements. It is obvious that the atomistic approach is the more reasonable one in dealing with vibrations of very high frequencies, and that it is much more likely to give us the correct results.

The immense numbers of atoms involved and the complexity of the structure of many crystals might suggest that the atomistic approach to our problem would be a formidably difficult one. Actually, however, this is not the case. A very great simplification is introduced by the fact that all crystals consist of a finite number (in many cases quite a small number) of sets of equivalent atoms. Equivalent atoms have the same mass and occupy equivalent positions in the structure of the crystal. They are held in their respective environments by equivalent force-systems. In any particular mode of vibration, all the atoms must oscillate with the same frequency and with either the same or the opposite phases everywhere. The forces acting on any given atom are determined by its own displacement and by the displacements of the atoms forming its environment. These factors in the problem result in a severe restriction of the possible modes of atomic vibration. It is easily seen that the conditions stated can only be satisfied if the resultant force acting on an atom and its consequent displacement have the same magnitude and either the same or the opposite phase as the corresponding quantities for every other equivalent atom. This again is only possible if the amplitudes and phases of atomic vibration repeat themselves in a space-pattern of which the units have twice the linear dimensions and, therefore, eight times the volume of the unit cell of the crystal lattice. This doubling of the scale of the vibration pattern as compared with the static structure of the crystal is a direct consequence of their being two possibilities for the relative phases of the movements of neighbouring equivalent atoms in the crystal, namely, that they may be either the same or the opposite of each other.

The atoms whose movements describe the possible modes of atomic vibration are thus eight times as many as those included in the unit cell of the crystal lattice. Multiplying their number by a factor of three representing the degrees of freedom of movement of each atom, and subtracting from the total, the three possible movements of translation of the entire group, we get $(24p - 3)$ as the number of its possible internal modes of vibration, p denoting the number of sets of equivalent atoms in the crystal. Of this total, $(3p - 3)$ vibrations are movements of the various interpenetrating lattices of atoms as a whole with respect to each other, while the remaining $21p$ vibrations are oscillations in which the alternate planes of equivalent atoms in the crystal oscillate against each other. These numbers are very greatly reduced when the crystal possesses a high degree of symmetry, as for instance, when it belongs to the cubic, tetragonal or hexagonal class, several of the possible modes of vibration then becoming identical. The existence of symmetry also enables us in many cases to specify the directions of movement of the atoms in the crystal. A complete enumeration and geometric description of the various possible modes of vibration is, in fact, possible in the case of crystals of high symmetry and of not too complicated a structure.

The ideas and results briefly outlined here are elaborated and applied to several different crystal structures in a symposium of papers published as the November 1943 issue of the *Proceedings* of the Academy. Taking, for instance, the cases in which the crystal contains only one species of atom, Mr. G. N. Ramachandran has systematically dealt with all the fourteen possible space-lattices in turn, and showed how the number of possibilities diminishes from the 21 modes of vibration with unspecifiable directions for the triclinic lattice to the four modes with completely defined directions of the face-centred and body-centred cubic lattices. The cases of various structure types in the cubic system, *e.g.*, rock-salt, zinc blende, flourspar and cæsium chloride, have been discussed by Mr. E. V. Chelam both by purely geometric and by group-theoretical methods. The application of the analytical methods of the group theory to the problem has been considered in the symposium from two different points of view. One way is the application of the standard group-theoretical methods to the enlarged space-unit containing eight lattice cells. The other is to start with each of the eight possible classes of vibration for the unit cell of the crystal lattice shown to be possible by the dynamical theory and consider them in turn. It is very gratifying that the results obtained by Professor Bhagavantam and Mr. Chelam respectively by the two methods in the case of diamond are completely identical. They show that the diamond structure has eight fundamental frequencies of vibration, of which the highest represents an oscillation of the two interpenetrating lattices of carbon atoms against each other. Their theoretical investigations enable us to understand the very striking experimental results obtained by Nayar in his studies of the luminescence and absorption spectra of diamond at low temperatures, as also the experimental findings of Dr. R. S. Krishnan in his recent investigations on the scattering of the 2,537 mercury radiations in diamonds of the ultra-violet transparent type.

Considered broadly, the results of the present theory form a striking and even startling contrast with those generally believed in at present. We see that the atomic vibration-spectrum of a crystal is essentially discontinuous and exhibits a finite set of discrete monochromatic frequencies, which are the more numerous, the more complicated the structure of the crystal is and the lower its symmetry. This picture bears no resemblance to the older ideas of the vibration spectrum of a crystal suggested by an extrapolation from the theory of the elastic vibrations of a solid. Such extrapolation into the region of atomic vibration frequencies is the basis of the well-known theory of specific heats of solids due to Debye; it yields an immense number of frequencies forming a continuous spectrum, in which the modes of vibration aggregate more densely together as we approach the high-frequency limit assumed in the theory. The Born crystal dynamics also yields a continuous spectrum of vibration frequencies as the result of the assumption on which it is based, namely, the Born-Karman boundary conditions, also known as the postulate of the cyclic lattice. The difference between the results of the new

crystal dynamics and of the existing theories is so great that the issue between them ought to be capable of settlement by a direct appeal to the experimental facts. The relevant spectroscopic evidence has been marshalled in two reports by Dr. R. S. Krishnan and by Mr. D. D. Pant, dealing respectively with the scattering of light in crystals and with their luminescence spectra and the associated absorption spectra at low temperatures. As will be seen from the reports, these three entirely independent groups of experimental studies furnish a great mass of unequivocal and by reason of their concurrence, overwhelming evidence that the vibration spectra of crystal lattices consist of discrete monochromatic frequencies which under ideal conditions, *e.g.*, at low temperatures, are quite as sharply defined as the vibration-frequencies of a gaseous molecule.

The failure of the Born dynamics to explain the observed facts is perhaps most clearly evident in the very case which has been most exhaustively discussed by Born and his collaborators, namely, rock-salt. The vibration-spectrum of the sodium chloride structure has been worked out on the basis of the Born postulate by Kellermann, and is a continuous one with three very broad and diffuse humps or intensity-maxima. On the other hand, in the present theory, the structure has 'one discrete frequency of vibration representing the oscillation of the sodium and chlorine lattices against each other, and eight other discrete frequencies representing oscillations of the layers of atoms parallel to the cubic and the octohedral planes alternately against each other in specifiable directions. On account of the symmetry of the atomic arrangements in the crystal, all the nine frequencies are inactive as fundamentals in light-scattering. The theory, however, indicates that all the nine frequencies may appear as octaves in the spectrum of the light scattered by the crystal. As long ago as 1931, using the 2,537 radiations of the mercury arc, a large clear rock-salt crystal, and prolonged exposures, Rasetti obtained a very beautiful spectrogram and microphotometric record. This appears very clearly reproduced in Fermi's book of 1938 entitled *Molekule und Krystalle*. Fermi himself admitted his inability to offer any explanation for the features very clearly observed in Rasetti's spectrogram. On the other hand the present theory offers a natural and convincing explanation of Rasetti's results, as has been shown by Dr. R. S. Krishnan in his report. The spectrogram and microphotometer record alike show the nine distinct frequencies required by the new dynamics of crystal lattices, quite clearly resolved from each other.

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The success of the new crystal dynamics in offering a simple and natural explanation of a great body of spectroscopic facts shows that it rests on sound foundations. Various subsidiary issues, however, arise which require to be investigated in detail. One of these is the question, are there possible modes of vibration in which the space-units of the repeating pattern contain larger numbers of lattice cells than the eight indicated by the theory? Such a possibility was envisaged by me in a paper published in the *Proceedings* of the Academy two years ago. It is readily seen, however, that all modes of vibration in which equivalent atoms have the same amplitude of vibration are included in the theory already indicated. On the other hand, if the amplitudes are different, and the vibration pattern is on a larger scale, its modes and frequencies should be capable of being described, at least as a rough approximation, by the ordinary ideas of the elastic solid theory. Hence, we are justified in ignoring all such possibilities in a treatment of the vibration problem on a purely atomistic basis. That we have to exclude the three degrees of freedom of translation of the whole group of atoms in our enumeration of their possible modes of vibration is, however, a clear indication that there are other possible modes of vibration of the crystal lattice. It is *a priori* evident that these would be of lower frequencies and would closely resemble elastic vibrations of very small wave-lengths. The investigation of such modes of vibration is not without importance when we seek to apply the ideas of the new crystal dynamics to various problems, especially the calculation of the specific heats of the simplest types of crystal at the lowest temperatures.

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The basis of our discussion so far is the classical mechanics, coupled with the idea that in considering the modes of atomic vibration in the interior of a crystal of macroscopic size, the conditions at the external boundary of the crystal are irrelevant. The agreement of the results of the theory with the experimental facts shows that such disregard of the boundary conditions at the surface of the crystal is justified. It indicates also that the various possible atomic states within a crystal are to be described in terms of space-units which are either the lattice spacings of the crystal, or integral multiples thereof and not in terms of sub-multiples of an arbitrarily assumed external dimension of the solid. We are naturally led to ask, should not similar ideas be extended to other aspects of the subject of crystal physics, including especially the theory of the electronic constitution of solids? The discussion which has been organised on this subject, and of which Professor K. S. Krishnan is the opener, may perhaps help to clarify the position of the latter problem and point the way to new and significant advances in our fundamental knowledge of the crystalline state of matter.