

NEW CONCEPTS OF THE SOLID STATE*

BY SIR C. V. RAMAN

MY first duty is to thank the authorities of the Nagpur University on behalf of the Indian Academy of Sciences for the invitation which has enabled the Annual Meeting of the Academy to be held this year under the auspices of the University. The Fellows of the Academy deeply appreciate the labours of the Chairman and members of the local Committee and of Prof. Moghe in making the arrangements for the meeting and are grateful for the hospitality which has been generously provided for the occasion.

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For good or for evil, we live in an age of science. No one who is familiar with the history of science would fail to recognize the great influence which has been exercised on its progress by the work of the various national academies of science, as for instance the Royal Society of London and the Academy of Sciences at Paris. The publications of these academies are the primary records of scientific discovery and invention in their respective countries. To no small extent, also, the Academies have been responsible for the promotion and encouragement of research work and for the co-ordination of the research activities of the Universities. During the seven years the Indian Academy of Sciences has been in existence, it has striven to fulfil these functions in our country. The *Proceedings* of the Academy which have appeared punctually, month after month, embody the best part of the research work done in most of the Indian Universities. It is greatly to be desired that these Universities appreciate what the Academy is doing for them and help the Academy to carry on under the present difficult conditions.

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I propose to devote my address this year to an exposition of the new ideas concerning the solid state of matter which have emerged from recent investigations made at Bangalore. The vast majority of actual solids are crystalline in structure and are either single crystals or else consist of polycrystalline aggregates. The gateway to an understanding of the solid

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state is therefore to be found in the study of crystals. The most effective starting point for such a study is, again, the ultimate structure or atomic architecture of the solid. The physics of the solid state of matter indeed concerns itself largely with the relationship between the atomic grouping in space which characterizes a crystal and the physical behaviour of the solid in various circumstances.

As is well known, crystals often possess beautiful external forms with specific geometric features. The symmetry characters of these geometric forms stand in the closest relation to the physical properties of the solid, such relationship being most evident when we consider those properties which vary with direction. The study of the geometric forms and of the physical properties of crystals resulted in the classification of crystal forms into six or seven systems and their further sub-division into thirty-two classes of crystal symmetry. It is natural that crystallographers were led by such studies also to speculate on the features in the internal architecture of crystals to which could be ascribed the external symmetry properties manifested by them. The theoretical investigations which dealt with this problem resulted in the recognition that a crystal is essentially a repetitive pattern in space and that the material particles of the solid are arranged in regular geometric order in a three-dimensional space-lattice. The discovery of the 14 possible kinds of space-lattice and of the 230 possible ways of grouping the atoms, each in its own appropriate type of space-lattice and coming under one or another of the 32 possible symmetry classes, gave the necessary precision and completeness to such general notions of crystal architecture.

The ideas of the mathematical crystallographers of the nineteenth century found a spectacular confirmation in Laue's great discovery made in 1912 of the diffraction of X-rays by the space-lattice of crystals. During the thirty years which have elapsed since that discovery, a vast amount of detailed knowledge regarding the structure of individual crystals has been built up by the labours of the X-ray crystallographers. Around such knowledge, again, there has been a great deal of discussion regarding the nature of the forces which held together the atoms, ions or molecules in a crystal in the form of a coherent solid.

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It must be recognized that the concept of a regularly ordered assemblage of atoms, ions or molecules in a space-lattice is only a static description of crystal structure and does not suffice to give a complete view of the solid state. That the density and many other physical properties of

a solid vary with temperature is clear indication that the atomic positions in a crystal are subject to disturbance by thermal agitation. A description of the possible atomic movements in a crystal is thus as important for crystal physics as a knowledge of the static structure. In other words, a dynamic picture of the crystalline state is required as a complement to the static picture furnished by the space-group theory. The possible modes of atomic vibration would evidently be determined by the atomic groupings in the crystal lattice and the forces that come into play when such grouping is disturbed. It follows that the static and dynamic aspects of crystal architecture should stand in the closest relationship to each other.

A dynamic concept of the solid state is necessarily the starting point in any consideration of the thermal properties of a crystal, *e.g.*, its specific heat, thermal expansion or thermal conductivity. It is equally fundamental in any attempt to elucidate such physical properties of solids as are notably influenced by temperature, *e.g.*, the electrical resistivity of metals. The subject of crystal dynamics assumes a special importance in considering the effects arising from the propagation of electromagnetic waves through crystals, *e.g.*, the scattering of light or the diffraction of X-rays. Spectroscopic and X-ray studies on crystals indeed afford us a penetrating insight into the problems of the solid state.

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The theorists who have handled such problems in the past have proceeded by carrying over notions derived from the classical theory of vibrating elastic solids into the domain of atomic dynamics. The history of physics during the present century suggests that all such extrapolations from macroscopic to atomic concepts must be regarded with caution. The extrapolations made in the Debye and Born theories of crystal dynamics do not, however, appear to be justified even from a purely classical point of view. It is not surprising, therefore, that the conclusions derived from these theories fail to survive the test of comparison with the experimental facts in several different branches of research. Before we proceed to consider evidence of this kind, it appears desirable to examine the foundations on which these theories rest.

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We may, in the first instance, comment on the well-known specific heat theory of Debye which has had the run of the text-books of physics for many years and even yet seems to be in favour. The theory assumes that the thermal energy of a solid may be identified with the energy of elastic waves travelling within it, and gives an expression for the energy in terms

of the velocities of these waves. That these assumptions are unjustifiable is evident from Debye's own formulæ. For, the calculation shows that a very large proportion of the elastic vibrations must be assumed to possess wave-lengths comparable with the lattice spacings of the crystal. Their frequencies also become comparable with those of the vibrations of the individual atoms. Even according to the classical principles, vibrations of such short wave-lengths and high frequencies could scarcely be expected to travel through the crystal with the assumed acoustic velocities. Indeed, the familiar fact that thermal energy does not travel at all but only diffuses with extreme slowness in solids is a clear disproof of the basic assumptions of the Debye theory. Far from supporting the postulates of the theory, the facts point to exactly the opposite conclusion, namely that no sensible part of the thermal energy of solids consists of the elastic vibrations of macroscopic physics.

The so-called postulate of the "cyclic lattice" on which the crystal dynamics of Born is based was introduced by him as a mathematical device to escape the difficulties which he believed to arise from the unspecified conditions at the external boundary of the crystal. The postulate in effect prescribes "wave-lengths" for the atomic vibrations in the crystal which bear no relation to its internal architecture but are related to its external dimensions in exactly the same way as the elastic vibrations of macroscopic physics. The postulate of the cyclic lattice has no theoretical justification and its introduction makes Born's approach to the problem of crystal dynamics wholly unreal and no less open to criticism than the theory of Debye.

The fallacy of the basic ideas underlying the Debye and Born theories becomes evident when we consider the nature of the vibrations within a solid indicated by the classical theory of elasticity. The form and size of the external boundary of the solid determines the possible modes of elastic vibration. In each individual vibration, the motion at all points within the solid has a specifiable frequency and a coherent phase-relationship. But there would be an immense number of such modes with varying frequencies. The superposition of all such modes, assumed to be co-existent, would therefore result in the agitation within the solid being of a completely chaotic character, varying from point to point and from instant to instant without any recognizable periodicity in space or recurrence in time. Thus, in effect, the assumptions made in the Debye and Born theories are equivalent to the assertion that while the static arrangement of the atoms in a crystal is one of perfect order and regularity, the dynamic character of their movements is one of perfect chaos and disorder, indeed exactly of the same

kind as the movements or vibrations of the molecules of a gas. This conclusion is obviously so improbable that we may well feel justified in rejecting without hesitation the premises on which it is based.

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A crystal, as we have seen, is a periodic array of similar particles, similarly situated and capable of influencing each other's movements. It follows that the vibrations of such an assemblage should exhibit a high degree of orderliness, approaching the ideal of a perfectly co-ordinated vibration in which the frequency, amplitude and phase are identically the same throughout the crystal. To picture such a vibration, we may first consider the group of the atoms present in an individual cell of the space-lattice. The internal vibrations of such a group would comprise several distinct modes determined by the number of atoms present. Each such vibration may then be pictured as occurring in identically the same way in every cell of the crystal lattice. Geometrically, such an oscillation could be represented as a periodic movement, relative to each other, of the interpenetrating simple lattices of similarly placed atoms of which any crystal may be regarded as built up. Such a vibration would have a uniquely definable frequency, and the vibration spectrum of the crystal would therefore consist of a finite number of discrete monochromatic frequencies.

Thus, instead of an infinite array of chaotic movements varying arbitrarily in phase from cell to cell of the crystal, and having a continuous spectrum of frequencies, we obtain a finite group of vibration modes with space-patterns coinciding with the lattice structure of the crystal and having a set of discrete monochromatic frequencies. These vibrations are essentially periodic changes in the fine structure of the crystal and do not involve mass movements of the substance of the solid. Hence, neither the existence of an external boundary nor the conditions restraining its movements can have any influence on such vibrations.

The most appropriate choice for the space unit of the three-dimensional repetition-pattern of the atomic vibrations is evidently that which enables all the modes possible to be included without redundancy. Hence the appropriate choice is not the cell having the smallest dimensions or including the least number of atoms, but one which is fully representative of the crystal structure and symmetry. In the majority of crystals, the number of atoms included in such a space-unit would be fairly large. Hence, the internal vibrations of the group of atoms contained in it would comprise the largest proportion of the available degrees of freedom of movement, indeed all except a small residue representing the translatory movements

of the chosen cell. To enable these latter to be included in the scheme, we may consider the internal vibrations of a group of atoms contained in the cells of a super-lattice having cells of twice the linear dimensions and therefore of eight-fold volume. Proceeding in this way by successive steps, the vibration spectrum of the crystal could be developed with all desirable completeness as a set of monochromatic frequencies.

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It will be realised that the geometric characters as well as the frequency distribution of the atomic movements in crystals obtained in this way would be radically different from those indicated by the Debye and Born theories. It is evident also that the new concepts involve striking differences in the spectroscopic, X-ray and thermal behaviour of crystals as compared with those derived from the older ideas. The issues arising between the new and the older concepts are thus capable of being brought to an exact experimental test.

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The atomic vibrations in crystal lattices are accessible to optical and spectroscopic investigation in several different ways. A method which makes the entire frequency range conveniently accessible to observation is the spectroscopic study of the scattered radiations emerging from a crystal traversed by monochromatic light. The most striking feature revealed by such studies with crystals is the extreme sharpness of the displaced lines appearing in their spectra. Even in those cases where the lines are somewhat diffuse, they sharpen into the finest lines when the crystal is cooled down to low temperatures. The monochromatism of the lattice frequencies thus indicated is especially significant when the vibrations are observable only in the crystalline state, in other words when the lines disappear in the molten or dissolved material. These facts are wholly inconsistent with the Debye and Born theories. Indeed, it may be said that the character of the spectra observed even with the simplest of crystals bears no resemblance to the diffuse continua suggested by these theories. Evidence confirmatory of the new concepts of crystal dynamics is also furnished by the absorption and luminescence spectra of crystals observed at low temperatures, *e.g.*, diamond. Here again, the lattice spectrum is revealed as a set of discrete monochromatic frequencies stretching down to low values, in startling contrast with the conclusions of the Debye and the Born theories.

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As already explained, the new concepts indicate a close correspondence between the static structure and the dynamic behaviour of a crystal,

in other words that the atomic vibration patterns are either identical with or closely related to the lattice structure of the crystal. As an immediate consequence of this relationship, it follows that the lattice planes of a crystal should give two distinct types of X-ray reflection—a dynamic reflection with altered frequency in addition to the static reflection of unmodified frequency discovered by Laue. The more perfectly co-ordinated is the oscillation of the lattice structure, the more perfect would be the geometric character of the dynamic X-ray reflections. Hence, these reflections should be shown in the most striking way by diamond-like structures in which the entire crystal is practically a single molecule and less perfectly by other crystals in which the lattice structure is of a more open kind.

That the lattice planes in crystals do give the new type of dynamic X-ray reflection here indicated and that such reflections are incapable of being explained on the older theories was discovered and announced by myself and Dr. Nilakantan in March 1940. In a symposium of fifteen papers published in the *Proceedings* of the Academy for October 1941, the theory of these new X-ray reflections, their relation to quantum mechanics and the experimental facts as observed with diamond and numerous other crystals have been thoroughly explored. It has been proved that the experimental facts are, on one hand, fatal to the Debye and Born theories and that on the other hand, they give the strongest support to the new concepts of the solid state.

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To the pioneer investigations of Einstein, we owe the basic principles of the quantum theory of the specific heat of solids. He showed clearly that the thermal energy of a crystal stands in the closest relation to its optical properties and could, in fact, be expressed in terms of the characteristic frequencies of atomic vibration appearing in the infra-red region of frequency. In his earliest paper, Einstein suggested that the atomic frequencies could be assumed to be monochromatic. Considering one such characteristic frequency in the case of diamond, he evaluated the same from the specific heat data. It will be seen from our present discussion that the basic assumption of monochromatism was justified, and that the only amendment needed in Einstein's theory was the inclusion of the full number of discrete monochromatic frequencies demanded by the lattice structure of the crystal with the appropriate statistical weights. It is also seen that the application of the macroscopic theory of elastic vibrations due to Debye, successful though it seemed at the time, was, in reality, a false step.

In a symposium of seven papers published in the *Proceedings* of the Academy for November 1941, the problem of the thermal energy of crystalline solids has been discussed fully from the new point of view and compared with the experimental data for a variety of substances. In several cases where the necessary spectroscopic data were available, these have been effectively made use of. In other cases, *e.g.*, metals, the specific data themselves have been utilised to evaluate the atomic frequencies. The most significant fact which emerges from the symposium is that the experimental facts in several cases which refused obstinately to fit into the Debye and Born theories find a natural explanation in the new concepts without the aid of any special hypothesis.

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Summary

The postulates on which the Debye theory of the specific heat of solids and the Born crystal dynamics are respectively based have been critically examined and shown to be theoretically untenable. Since a crystal is a three-dimensionally periodic grouping of similar oscillators coupled together, it follows that the modes of vibrations possible would be also space-periodic, the geometric modes being determined by the characters of the atomic space-grouping in the crystal. They would further form a finite and enumerable set of monochromatic frequencies. The spectroscopic, X-ray and thermal behaviours of a crystal would on these views be radically different from those consequent on the Debye and Born theories. The experimental facts are found to contradict the conclusions of these theories and on the other hand, to be in full accord with the new concepts.