The thermal energy of crystals*

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The determination of the nature of the atomic movements which constitute the thermal agitation in a crystal is a fundamental problem in the physics of the solid state. Its importance will be evident when it is remarked that even the most familiar aspects of the thermal behaviour of solids depend for their explanation on the precise nature of these movements. The subject also stands in the closest relationship with the spectroscopic behaviour of crystals and with X-ray crystallography, to say nothing of various other branches of physics.

Since the atomic movements under consideration are of thermal origin and are presumably in the nature of vibrations about the atomic positions of equilibrium, the subject has to be viewed in the light of the fundamental principles of thermodynamics and the quantum theory. However, as in the parallel problem of the vibration spectra of molecules, we have to seek the aid of classical mechanics for ascertaining the modes and frequencies of vibration with which we are concerned.

2. Thermodynamic considerations

Every crystal is a three-dimensional grouping in space of atoms held together by their mutual interactions; equivalent atoms in the crystal are located at the points of a Bravais lattice, and if the crystal consists of p interpenetrating Bravais lattices, there would be p atoms in each unit cell of the crystal structure. Since the frequencies of vibration of the atoms are determined by their masses and by the interatomic forces which are of limited range, they would necessarily be the same for the group of atoms contained in every cell of the structure. Hence every crystal may be considered as an assembly of a great number of oscillators physically similar to each other and having a set of vibration frequencies in common, and which since the oscillators can exchange energy with each other, constitute a system in thermodynamic equilibrium. Each oscillator can for any particular frequency of vibration assume any of the energy states permitted by the quantum

theory, the probability of its being present in any one state being given by Boltzmann's well known formula. The energy of the entire assembly of oscillators can therefore be evaluated by multiplying the number of oscillators of any particular frequency by the average energy of an oscillator of that frequency which is calculable from the relative probabilities of its different energy states, and then summing up the results for all the frequencies. The total number of oscillators included in such a reckoning would be three times the number of atoms comprising the crystal. This follows from the theorem in classical mechanics which states that the number of normal modes of vibration of a connected system of particles is the same as the number of degrees of freedom of movement of the entire system.

3. Dynamical theory

The dynamics of atomic vibration in a crystal may be dealt with from two different standpoints which may be designated as the "molecular" and "molar" points of view respectively. In the "molecular" approach to the problem, we fix our attention on a particular unit cell of the crystal structure and proceed to write down and solve the $3p$ equations of motion of the p atoms contained in it, with a view to discover and enumerate their normal modes of vibration. In doing this we have necessarily to take account of the forces arising from the movements of the atoms in the surrounding cells which interact with those in the cell under consideration. It is obvious that no mode of vibration of the atoms in the unit cell can persist unchanged unless the atoms in the surrounding cells also vibrate in a similar mode with the same frequency. This would be the case if equivalent atoms in these outer cells also vibrate with the same amplitudes, but as regards their phases of vibration, there are several distinct possibilities. A formal investigation shows that there are $2 \times 2 \times 2$ or eight possibilities in all which can be described as follows: The phases of equivalent atoms are either the same or else opposite in consecutive cells along one, or two, or all the three axes of the Bravais lattice. The identity of the amplitude of vibration of equivalent atoms reduces the number of independent co-ordinates to $3p$ only. Thus, the equations can be solved and result in $3p$ solutions, but as there are eight different situations in respect of the phases, we have $8 \times 3p = 24p$ solutions in all. This is the same as the number of degrees of dynamic freedom of the $8p$ atoms contained in a super-cell having twice the linear dimensions of the unit cell of the crystal structure. Accordingly, we recognize $(24p - 3)$ normal modes of vibration properly so-called, the three omitted degrees of freedom representing the translatory movements of the super-cell.

In the "molar" approach to the problem, we consider the entire crystal as a single physical entity and investigate the propagation of waves through its structure. The wave equations are found to be formally satisfied if it be assumed that the equivalent atoms located at the points of a Bravais lattice have the same

amplitude of vibration, this however being different for the different lattices of atoms, while the frequency, wavelength and the direction of the wave-vector are the same for all the interpenetrating lattices. Proceeding to solve the set of $3p$ equations obtained on this basis, an algebraic equation of degree $3p$ for the frequency results, and the solution of this gives us $3p$ different frequencies for a wave of given wavelength travelling in any assigned direction. By considering the functional dependence of these $3p$ frequencies on the wavelength and direction of propagation, it is found that the group-velocity of the waves vanishes for $(24p - 3)$ frequencies associated with eight different wave-vectors in the crystal. The $(24p - 3)$ frequencies thus obtained and the corresponding modes of vibration are found to be the same as the frequencies and normal modes deduced by the "molecular" approach to the problem, namely, those in which equivalent atoms in consecutive cells vibrate with the same amplitude and with phases that are either the same or else opposite along one, two or all three of the Bravais axes of the crystal. They may therefore be identified as the characteristic or normal modes and frequencies of vibration of the crystal structure. The three omitted frequencies represent the limiting case of the three sets of waves of the lowest frequencies and the longest wavelengths for which the group velocity does not vanish but comes out as equal to the phase-velocity of the waves. These cases are identifiable with the three types of waves whose propagation in any direction in the crystal is shown to be possible by the classical theory of elasticity. The vanishing of the group velocity for all the $(24p - 3)$ frequencies characteristic of the lattice structure is significant. It indicates that no wave-propagation in any real or physical sense is possible in a crystal except in the lowest range of frequencies where alone the ideas and results of the classical theory of elasticity possess any validity.

4. The spectrum of the thermal agitation

The results of the dynamical theory enable us to complete the thermodynamic picture already indicated above in outline. The p interpenetrating Bravais lattices of atoms constituting the crystal represent an assembly of atomic oscillators which have a set of $(24p - 3)$ vibration frequencies in common. Each of these oscillators can assume one or another of the various energy states for these frequencies permitted by the quantum theory, the relative probabilities of the same being given by the Boltzmann formula. It would not be possible to specify or predict which of the great number of oscillators in the crystal would be in a particular excited state for any of its possible frequencies of vibration at any given instant. In other words, the thermal energy would be distributed through the volume of the crystal in a manner which fluctuates from place to place and from instant to instant in an unpredictable fashion. The fluctuating character of the energy distribution would be the more striking, the higher the frequency under

consideration, since the energy jumps indicated by the quantum theory are proportional to the frequency.

Thus, it emerges that $(24p - 3)$ out of every $24p$ degrees of freedom of atomic movement in the crystal manifest themselves in the thermal agitation as modes of internal vibration with a precisely defined set of monochromatic frequencies and in modes specifically related to the crystal structure, though they are localised in the crystal in a chaotic and unpredictable fashion. The residual 3 degrees out of every $24p$ degrees of freedom represent, as we have seen, the translatory movements of the super-cells of the crystal lattice. Such movements would disturb the regularity of the crystal structure, in other words, would give rise to stresses and strains of the same general nature as those contemplated in the classical theory of elasticity. Hence, the 3 residual degrees of freedom would also manifest themselves in the thermal agitation as oscillations localised in the crystal in a chaotic and unpredictable fashion, but since the moving masses are now larger, the frequencies would necessarily be lower, being determined by the dimensions of the volume elements which can be regarded as the individual oscillators: the larger these volume elements are, the fewer of them would be needed to fill the crystal and the lower also would be the frequency. Thus, the spectrum of the thermal agitation resulting from movements of the kind under consideration would stretch over a range of frequencies down to low values, but the upper parts of the range would be much more densely populated than the lower.

5. Remarks on some earlier theories

The attentive reader would have noticed that the picture of the thermal agitation in a crystal and its spectroscopic characters which has emerged bears no resemblance whatever to that figuring in the well known theory of the specific heat of crystals put forward by Debye and in the lattice theory of Max Born and his collaborators. These authors identify the energy of the thermal agitation in a crystal with the energy of an immense number of waves traversing the crystal in all possible directions and of which the frequencies are all different. But nevertheless in evaluating the total energy, these authors make use of the expression for the average energy of an oscillator derived by Einstein for an assembly consisting of an immense number of oscillators having an identical frequency of vibration. In the circumstances, it would not be superfluous to set out briefly the considerations which show that the theories of Debye and Born are fundamentally misconceived and that the conclusions to which they lead are completely unreal.

I. The theory of the specific heat of crystals has necessarily to be based on the theorem in classical mechanics which states that the normal modes of vibration of a connected system of particles form an enumerable set equal in number to the

number of degrees of dynamical freedom of the system and that in each such normal mode, all the particles vibrate with the same or opposite phases. Waves are not normal modes, since the phase alters progressively in the direction of the wave-vector, and hence it is an obviously fallacious procedure to seek to found a theory of specific heat on the basis of wave-motions.

II. A dynamical investigation shows that waves of the kind contemplated by the classical theory of elasticity in which the phase-velocity is equal to the group velocity are only possible in the limiting case of very low frequencies and of very great wavelengths. It also shows that the atoms in a crystal form an assembly of oscillators which have a set of $(24p - 3)$ vibration frequencies common to all, and hence form a system to which the principle of Boltzmann can be legitimately applied to determine the average energy of an oscillator of each frequency and thereby to evaluate the total energy of the system.

III. The fundamental principles of thermodynamics and the quantum theory indicate that the thermal agitation in a medium consisting of material particles capable of vibrating about their positions of equilibrium is of a chaotic and unpredictable character, exhibiting fluctuations in the energy of the vibration from place to place and from instant to instant whose magnitude is determined by the frequency of vibration and hence would be different for each different frequency. It would be patently absurd to identify such a disturbance in the crystal with waves of constant amplitude spread over its volume.

IV. The identification of the thermal energy of a crystal with the energy of waves traversing it in all directions and having frequencies all different from each other leads to a totally false picture of the spectroscopic behaviour of crystals, as is shown by several independent methods of experimental investigation. For instance, all crystals usually exhibit at room temperature and always when cooled down to low temperatures the sharply defined shifts of frequency in the spectrum of monochromatic light scattered by them, corresponding to each of the $(3p - 3)$ frequencies of the structure active in light-scattering. Significantly also, overtones and combinations of these $(3p - 3)$ frequencies and of the remaining $21p$ frequencies manifest themselves with observable intensity as sharply defined frequency shifts with many crystals.

V. That the identification of the thermal agitation in a crystal with waves traversing the solid is a misconceived idea is also apparent from the complete dissimilarity between heat energy and sound energy in their observable behaviour. The latter travels through a crystal with a velocity of some thousands of metres per second, while heat energy merely diffuses through it.