

The specific heats of crystalline solids: Part I

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A correct appreciation of the nature of the thermal agitation in a crystal is obviously of fundamental importance in the physics of the solid state. Closely related to it is the problem of evaluating the heat content of a crystalline solid as a function of the temperature. These topics have formed the subject of some recent studies by the present writer. From them has emerged a theory of the specific heats of crystalline solids which is both simple and comprehensive and which succeeds in establishing a quantitative relationship between the thermal properties and the spectroscopic behaviour of crystals and accounts for the facts of observation in both of these fields. It accordingly seems opportune to offer a connected review of the subject in which the basic principles are set forth as simply and clearly as possible.

2. Some general considerations

A crystal is an assembly of great numbers of atoms (of the same or of several different species) in a three-dimensionally periodic array in space. Macroscopically regarded, a crystal of finite size is a single physical entity; and those problems concerning its physical behaviour in which the discrete atomic structure does not need to be specifically considered can be dealt with on that basis. But neither the evaluation of the thermal energy of the solid nor the determination of its spectroscopic behaviour is a problem of that nature. For, the discrete atomic structure of the solid is the very essence of both of these problems and it must therefore form the basis of any theoretical considerations regarding them. It is therefore a misconceived and irrational procedure to assume—as is done in the theories of Debye and Born—the macroscopic crystal to be itself the oscillating unit whose modes and frequencies of vibration determine the thermal properties and the spectroscopic behaviour of the solid. While we have necessarily to reject such an approach as inadmissible, we are also precluded from assuming that the individual atoms in the crystal are the oscillators with which we are concerned. This is obvious, for the atoms in a crystal are linked together by forces of a physico-chemical nature and hence they cannot oscillate independently of each other. Thus, when both of these extreme suppositions are laid aside, we are left with the following questions requiring an answer. What are the oscillators which

determine the thermal properties and the spectroscopic behaviour of a crystal? How are they to be enumerated, and in what manner are their modes and frequencies of vibration to be determined? The answers given to these questions stand at the very base of the problems now under consideration.

3. The normal modes of vibration

The fundamental theorem in classical mechanics regarding the small vibrations of a system of connected particles, taken in conjunction with the three-dimensional periodicity of structure characteristic of the crystalline state, furnishes us with the key to the solution of our problem. The theorem referred to states that the possible vibrations of the system are superpositions of a set of normal modes, in each of which the particles of the system (in the present case, the atoms) vibrate with the same frequency and in the same or opposite phases. Hence, any mode of vibration which satisfies this description and which can be regarded as a characteristic property of the crystal must also satisfy the further criterion that it remains the same when the crystal is given a unit translation along any one of the three axes of its structure. This can obviously happen in two ways: following the unit translation, equivalent atoms in the adjacent cell retain their amplitudes and phases of vibration unaltered, or alternatively, while the amplitudes remain the same, the phases are all reversed. Thus, we have $2 \times 2 \times 2$ or 8 different possible situations. If there are p atoms in each unit cell of the crystal structure, each of the 8 possible situations give us $3p$ solutions of the equations of motion of the p atoms in the unit cell, in other words, indicates $3p$ normal modes of vibration with their respective frequencies which can be regarded as characteristic of the structure of the crystal. Thus, in all, we have $24p$ solutions of the equations of motion which may be divided into three groups: $(3p - 3)$ normal modes in which equivalent atoms in adjacent cells oscillate with identical amplitudes and phases; $21p$ other normal modes in which the amplitudes of equivalent atoms in adjacent cells are the same but their phases alternate along one, two or all three of the axes of the crystal structure; and finally, the 3 excluded translations.

4. The oscillators and their enumeration

We proceed to consider the physical significance of the results deduced and stated above. What they indicate is that we shall not be justified in identifying the groups of p atoms each which form the units of the crystal structure as the "oscillators" in specific heat theory, since their juxtaposition in the ordered structure of the crystal results in an eight-fold increase in the number of distinct frequencies of internal vibration which these groups of p atoms each would possess if isolated

from each other. We have also to recognize the existence of additional modes of vibration within the crystal made possible by the translatory movements of the atomic groups as distinct from their internal vibrations. It is to be remarked, however, that the $(24p - 3)$ normal modes of vibration with discrete frequencies indicated by the theory can be regarded as the *internal* modes of vibration of the groups of $8p$ atoms each to be found in volume elements whose dimensions are twice as large in each direction as those of the unit cells of the crystal structure. If the entire crystal encloses N unit cells, the number of groups of $8p$ atoms included in it would be $N/8$. Multiplying this by $(24p - 3)$ which is the number of their internal modes of vibration, and adding to the product the number of degrees of the translatory freedom of movement of the same groups, we recover $3Np$, which is the total of the number of degrees of freedom of atomic movement in the crystal.

5. The vibration spectra of crystals

Thus, the atomistic approach to specific heat theory leads us directly to a result which is of fundamental importance in relation to the spectroscopic behaviour of crystals, namely, that by far the largest proportion of the atomic degrees of freedom of movement in crystals is manifested in their vibration spectra as a set of discrete monochromatic frequencies $(24p - 3)$ in number, p being the number of atoms in the unit cell, only the three omitted translations manifesting themselves in what may be designated as the "residual spectrum" comprising the lowest frequencies of vibration and having a different character which we shall consider presently. The nature of the vibration spectrum of a crystal as stated above which is indicated by the theory might have been anticipated *a priori* on general grounds. For, a crystal comprises within itself an immense number of similar and similarly situated groups of atoms which would necessarily be of identical dynamical behaviour. Hence, the modes and frequencies of internal vibration of these groups would all be the same and would be a characteristic property of the crystal. The reason why we have $(24p - 3)$ discrete frequencies and not $(3p - 3)$ is also readily understood. The additional $21p$ frequencies arise because of the coupling of the oscillators located along each of the axes of the structure, an effect analogous to that observed in the simple case of two similar oscillators which when coupled to each other exhibit two distinct frequencies of vibration instead of only one.

We must now consider the nature of the "residual spectrum" briefly alluded to above. This spectrum embodies the oscillatory movements arising from the *translations* of volume elements of the crystal each containing $8p$ atoms; they may be described as *internal vibrations* in volume elements of still larger size and therefore having lower frequencies. The frequency ν of such a vibration can evidently range from a lower limit $\nu = 0$ to the upper limit $\nu = \nu_L$, ν_L being the lowest of the $(24p - 3)$ discrete frequencies of atomic vibration. The manner in

which the disposable $3N/8$ degrees of freedom would be distributed over this range of frequencies can be deduced by a very simple argument. The total number of volume elements of an specified dimensions included in the crystal, and therefore also the number of degrees of freedom represented by their *translations* would diminish in inverse proportion to the cube of their linear dimensions, while the frequencies of their *internal vibrations* would vary inversely as the first power of the same. Hence the number of degrees of freedom appearing in the residual spectrum in the range of frequencies between 0 and ν would be proportional to ν^3 . By differentiation, we obtain the result that the number of degrees of freedom appearing between frequencies ν and $\nu + d\nu$, in other words, the number of oscillators in the crystal having frequencies in that range, would be $3N/8 \times 3\nu^2 d\nu/\nu_L^3$.

6. Quantisation of the vibrational energy

In his classic paper of 1907 introducing the quantum theory of specific heats, Einstein showed that the acceptance of his theory of light quanta inevitably leads to the conclusion that the energy of the mechanical vibration of elementary oscillators—such as the molecules of a gas or the structural units in a crystal—would also be related to their respective frequencies by the quantum rules. He also indicated a procedure by which the thermal energy of a crystal could be evaluated as a function of the temperature on the basis of the quantum hypothesis. He identified the thermal energy of the crystal with the energy of mechanical vibration of an immense number of *individual* oscillators distributed over its volume. It was assumed that these oscillators could be grouped into sets, each set comprising a great number of individual oscillators characterised by a common frequency of vibration. The total number of the oscillators of all kinds was taken to be equal to thrice the number of the atoms comprised in the crystal. The oscillators themselves were assumed to be harmonic and to occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The thermodynamic principle of Boltzmann was then introduced, leading to the result that the numbers of the oscillators occupying the various permitted levels are in the relative proportions indicated by that principle, and determined by the respective energies and by the temperature. The average energy of the oscillators in each of the sets was then evaluated. Summing up over all the oscillators in each of the sets and then over all the sets, Einstein obtained an explicit formula for the thermal energy of a crystal as a function of the temperature.

Einstein's ideas necessarily form the basis of any rational approach to the solution of the specific heat problem for crystals. For, they are based on an atomistic approach to the problem and effect a synthesis of the results of classical dynamics with the notions of the quantum theory and the basic principles of thermodynamics, in other words, of all the three disciplines which find a place in

the problem Einstein's formulation, however, had the weakness that he left unanswered three important questions: What precisely are the individual oscillators contemplated in the theory? How are they to be enumerated? How should their frequencies of vibration be determined? Also to enable his theory to be applied in the particular case of diamond, Einstein assumed that the individual atoms in that crystal were themselves the oscillators contemplated in his theory. This was an oversimplification which resulted in discrediting Einstein's theory. For, that assumption was theoretically unsustainable and it also led to values for the specific heats at low temperatures which were in disagreement with the experimental facts elicited by later investigations. It is not surprising in these circumstances that Einstein's approach to the specific heat problem was laid aside, and that other and totally different ways of approaching the same problem gained general acceptance.

The present approach to specific heat theory is in a sense a rehabilitation of Einstein's original ideas. It fills in the lacunae left by him and we are thereby enabled to make use of Einstein's formulae just as they stand for an evaluation of the thermal energy of the crystal. But, before we proceed to write down the expressions, it appears desirable to emphasize certain fundamental aspects of Einstein's theory which also find a place in the present approach to the subject. Einstein's application of Boltzmann's statistical-thermodynamical principle finds its logical justification in the fact that the crystal is regarded as an assembly of great numbers of similar oscillators capable of exchanging energy with each other and forming a system in thermodynamic equilibrium. The use of the principle implies that the energy of vibration of the individual oscillators of each sort exhibits fluctuations over the volume of the crystal both in space and in time, the magnitude of these fluctuations being naturally the greater, the higher the frequency of the oscillator considered. This picture of the thermal agitation in crystals is fundamentally in accord with the actual facts of crystal architecture as well as with the principles of thermodynamics, but it is very remote indeed from any ideas of its nature based on the notions of macroscopic physics.

Another feature of Einstein's theory which he himself stressed is the intimate relationship which it indicates between the thermal properties and the spectroscopic behaviour of crystals. The same relationship is also a feature of the present theory. But, the latter goes further than Einstein's, since it specifies the number of sets of oscillators which are the carriers of the thermal energy and also indicates the procedure by which their frequencies may be evaluated. Properties descriptive of the macroscopic behaviour of solids, viz., their elastic constants, do not as such find a place in the present theory of the specific heats of crystals.

7. Evaluation of the specific heats of crystals

Making use of the reasoning employed by Einstein, we obtain the following expression for the heat content of a volume of a crystal containing N unit cells of

the crystal structure as a function of the temperature, namely

$$\frac{N}{8} \left[\sum_{i=1}^{24p-3} \frac{hv_i}{\exp(hv_i/KT) - 1} + \frac{3}{v_L^3} \int_0^{v_L} \frac{3hv^3 dv}{\exp(hv/KT) - 1} \right].$$

The numerical factor $1/8$ appears in the expression because each oscillator comprises 8 unit cells of the crystal structure. On differentiating the expression with respect to T , we obtain the formula for the specific heat.

The following remarks may be made regarding the numerical evaluation of the expression given above. All the $(24p - 3)$ frequencies would be distinct from each other only in the case of a completely anisotropic crystal. If any symmetry elements are present, the number of distinct frequencies would be naturally diminished, but the formula remains the same. Such reduction in the number of distinct frequencies would appear both in respect of the $(3p - 3)$ frequencies in which both the amplitudes and the phases are the same in adjacent unit cells and in the $21p$ others in which the phases may be opposite, as already explained. As an illustration of these remarks, we may consider a case in which $p = 2$ and the crystal belongs to the cubic class and its structure consists of two interpenetrating face-centred cubic lattices. The $(3p - 3)$ distinct frequencies then reduce to a single triply degenerate frequency; the $21p$ or 42 other vibrations reduce to only eight distinct frequencies, the modes relating to all of which may be readily described in geometric terms connected with the structure of the crystal.

Since the first term in the expression for the thermal energy is a summation extended over $(24p - 3)$ distinct modes of vibration, while the second represents the residual spectrum, it is evident that the latter would be of minor importance relatively to the first, especially in those cases where p is large, in other words when the crystal has a multi-atomic structure. The position is a little different when p is small, as for example, when p is equal to 1. The contribution from the second term would not then be altogether negligible in comparison with the first term. The second term also acquires some importance relatively to the first at very low temperatures. For, since the frequencies appearing in it are low, their contributions to the specific heat would survive when those due to the vibrations of the higher frequencies appearing in the first term have dropped out by reason of Boltzmann's principle.