

## The specific heats of crystals—Part I. General theory

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### 1. Introduction

The quantum theory of the specific heats of crystals proposed by Einstein in the year 1907 regards a crystal as an assembly of an immense number of harmonic oscillators with specific frequencies, the energy of vibration of which obeys the quantum rule; these oscillators form a system in thermodynamic equilibrium of which the behaviour can be described statistically with the aid of Boltzmann's theorem. Einstein identified these oscillators with the structural units ("Elementargebilde") in the crystal and assumed that they could be grouped into sets, each set comprising a great number of oscillators characterised by a common frequency of vibration; the total number of oscillators of all sorts is taken to be thrice the number of atoms comprised in the crystal. He showed it to be a consequence of his theory that the thermal properties of a crystal would stand in the closest relationship with its spectroscopic behaviour.

The assumptions on which Einstein's theory rests are clearly justified by the physical facts of the case. For, every crystal consists of an immense number of structural units similar to each other which are capable of mechanical vibration and which by reason of their similarity may be expected to exhibit identical dynamical behaviour. The theory is, in effect, a synthesis of the results indicated by classical dynamics for such a system with the notions of the quantum theory and the basic principles of thermodynamics. It involves no inherent contradictions and can therefore claim to be a rational approach to the fundamental problems of crystal physics. The following questions, however, need to be answered before any use can be made of the theory. How are the oscillators of different sorts envisaged in the theory related to the known structure of a crystal? How are they to be enumerated? What is the procedure by which the characteristic frequency of each set of oscillators may be evaluated? The present memoir concerns itself with finding the answers to these questions and thus giving form and substance to the ideas of a very general nature put forward by Einstein.

## 2. The normal vibrations of crystal structures

That the specific heat of a crystalline solid tends with rising temperature to reach a limiting value proportional to the number of atoms comprised in it is a clear indication that the theoretical approach to any explanation of the facts has of necessity to consider the subject from an atomistic standpoint. We have also to recognize the existence of interatomic forces; hence, the movements with which we are concerned are not simple translations of the individual atoms but vibrations of the atoms about their positions of equilibrium in the structure of the crystal. Any attempt to describe these vibrations or to enumerate them has necessarily to be based on the fundamental theorem in classical mechanics which states that all the possible small vibrations of a connected system of particles about their positions of equilibrium are summations of an enumerable set of normal modes; in each such normal mode the particles of the system have all the same frequency and the same or opposite phases of vibration. Hence, any rational approach to the specific heat problem must of necessity start with a consideration of the normal modes of vibration—in the sense of the theorem just stated—of the atoms about their positions of equilibrium in the lattice structure of the crystal.

The basic principle of crystal architecture is that the structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes into two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following a unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed and the normal mode therefore remains the same following the unit translation. Since these two alternatives are possible for a unit translation along each of the three axes of the lattice, we have  $2 \times 2 \times 2$  or 8 possible situations. Considering each of these situations separately, we proceed to write down the equations of motion of the  $p$  atoms comprised in the unit cell in terms of  $3p$  co-ordinates which determine their displacements. Since the displacements of the equivalent atoms in adjoining cells which interact with the atoms in the cell under consideration are also the same, the  $3p$  equations of motion of the latter contain only  $3p$  independent co-ordinates. They can therefore be completely solved, giving us  $3p$  solutions for each of the eight possible situations referred to above. Thus in all, we have  $24p$  solutions.  $(3p - 3)$  of these solutions represent normal modes of vibration of the first kind,  $21p$  solutions represent normal modes of the second kind and the three remaining solutions represent simple translations which have necessarily to be excluded.

The  $(24p - 3)$  normal modes of vibration of the atoms in a crystal indicated by

the theory may be regarded as the modes of *internal* vibration of the group of  $8p$  atoms comprised in a super-cell of the crystal lattice whose linear dimensions are twice as large as that of the unit cell consisting of  $p$  atoms. The three omitted solutions would then represent the translations along each of the three axes of the crystal lattice of the whole group of  $8p$  atoms included in the super-cell. Thus, we recognise that the structural unit whose dynamical behaviour is representative of the entire crystal is not the unit cell of the crystal structure, but has twice its dimensions along each of the three axes of the lattice.

Thus, following Einstein, we may regard a crystal as an assembly of  $(24p - 3)$  sets of oscillators, each of the sets having its own distinctive frequency of vibration. The number of oscillators in each set is the same as the number of super-cells containing  $8p$  atoms which are included in the whole crystal. Each set of oscillators forms an assembly in thermodynamic equilibrium and its behaviour can therefore be described statistically with the aid of Boltzmann's theorem. The average energy of an oscillator in each set is given by Einstein's formula for the particular frequency. Multiplying this by the number of super-cells contained in the volume of the crystal, we obtain an expression for the energy of all the oscillators in that set. Finally, summing up the expressions thus obtained for all the  $(24p - 3)$  sets with their respective frequencies of vibration, we obtain an expression for the thermal energy arising from the excitation of the vibrations of the atoms having precisely specifiable frequencies.

### 3. The vibration spectra of crystals

The foregoing results may be summed up as follows. If a unit volume of the crystal contains  $S$  super-cells each including  $8p$  atoms, the total number of degrees of atomic freedom is  $24pS$ ; a very large proportion of this number, viz.,  $(24p - 3)S$  degrees of freedom, appears in the vibration spectrum of the crystal as sharply defined monochromatic frequencies;  $(3p - 3)$  of these frequencies represent vibrations in which equivalent atoms contained in each super-cell have the same amplitudes and phases of vibration, while the  $21p$  other frequencies represent modes of vibration in which the amplitudes are the same but the phases are opposite for equivalent atoms along one, two or all three of the axes of the lattice.

We have now to consider and determine the nature of the movements represented by the  $3S$  degrees of atomic freedom left out in the preceding enumeration. This is also the number of degrees of freedom of translation of the  $S$  super-cells included in the crystal. Any translation of an individual super-cell would necessarily set up forces resisting such movement and also tending to displace neighbouring super-cells. We are therefore led to assume that the  $3S$  degrees of freedom under discussion would manifest themselves as internal modes of vibration in elements of volume of larger dimensions than our super-cell. The larger such element of volume is, the lower would be the limit of the possible

frequencies of such vibration. The translations of the individual super-cells are therefore to be associated with a whole series of frequencies lying between zero and an upper limit which is set by the frequency of internal vibrations in our super-cell. To take account of the anisotropy of the crystal, we would, in general, have to assume separate upper limits of frequency for the translations along the three axes of the crystal. It is left to determine how the  $3S$  unassigned degrees of freedom are distributed amongst the oscillators of various frequencies lying in the permitted ranges  $0 \rightarrow \nu_x, 0 \rightarrow \nu_y, 0 \rightarrow \nu_z$ .

The problem indicated above can be dealt with and solved in a very simple manner. Consider two volume elements in the crystal which have the same shape as our super-cell and whose dimensions are respectively  $m$  and  $n$  times larger. The number of degrees of freedom of translation of these enlarged super-cells is respectively three times the number of such cells included in the volume of the crystal; the difference between them, viz.,  $3S(1/m^3 - 1/n^3)$  would therefore be the number of oscillators whose frequencies lie between  $\nu_m$  and  $\nu_n$  which are respectively their lowest frequencies of internal vibration. But the principle of dynamical similarity enables us to write  $\nu_m = k/m$  and  $\nu_n = k/n$  where  $k$  is a constant having the dimensions of a frequency. Hence, as  $m$  approaches  $n$ ,  $\nu_m - \nu_n$  may be set equal to  $dv$  and the number of oscillators whose frequencies lie between  $\nu_m$  and  $\nu_n$  may be written as  $9S v^2 dv/k^2$ . On integrating this between zero and  $\nu_1$  (the upper limit of the permitted frequencies), we should recover  $3S$  as the total number of oscillators, and hence  $k^3$  is identified as  $\nu_1^3$ . Accordingly, the law of distribution of frequency in the spectrum may be written as  $9S \cdot v^2 dv/\nu_1^3$  for the isotropic case. More generally, for an anisotropic crystal  $\nu_1$  may be replaced by  $\nu_x$  or  $\nu_y$  or  $\nu_z$  respectively for the three directions of translations and the numerical factor 9 is replaced by 3.

The law of distribution of the frequencies thus derived indicates that the majority of the oscillators now under consideration have frequencies not far removed from the upper limit. The same result may be expressed otherwise by the statement that the majority of the oscillators are of very small dimensions not far removed from the lower limit, namely the dimensions of the super-cell. If, for example, we were to identify *all* the vibrations arising from the translations of the super-cell with the internal vibrations in a volume element whose dimensions are *twice* those of the super-cell, we would not be seriously in error. All except one-eighth of the  $3S$  degrees of freedom would be accounted for in such an enumeration; the residue omitted would represent oscillations in still larger volume elements appearing with still lower frequencies.

#### 4. The thermal energy of crystals

The atomistic approach to the specific heat problem proposed by Einstein, when fully developed, thus leads us to the following picture of the nature of the

vibrations in a crystal which are the carriers of the thermal energy. The oscillating units are *not* the unit cells of the structure, but are twice as large as the unit cells in their linear dimensions; their oscillations are of two kinds, namely, those arising from their internal vibrations and those arising from their translatory movements. The oscillations of the former description appear with  $(24p - 3)$  discrete frequencies of vibration,  $p$  being the number of atoms contained in the unit cells of the crystal structure. The translatory movements, on the other hand, appear with a spectrum of frequencies all of which are lower than those of the internal vibrations. These, for the most part, are concentrated near the upper limit of their permitted range; but there is a residue which tails off as a continuous spectrum to very low frequencies.

Accordingly, making use of the reasoning employed by Einstein for evaluating the average energy of an oscillator in each of the sets under consideration, 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

$$\frac{N}{8} \left[ \sum_{i=1}^{24p-3} \frac{hv_i}{e^{hv_i/kT} - 1} + \frac{3}{v_i^3} \int_0^v \frac{3hv^3 dv}{e^{hv/kT} - 1} \right]$$

The numerical factor  $1/8$  appears in the expression because each dynamic unit contains 8 unit cells of the crystal structure. On differentiating the expression with respect to  $T$  as usual, we get 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 and the formula would then contain only such smaller number, but the individual terms would then have to be multiplied by their respective degeneracies. Such reduction in the number of distinct frequencies would naturally 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, all of which may be readily described in geometric terms related to 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 only the three residual translations, it is evident that the latter would be of very minor importance relatively to the first, especially in those cases where  $p$  is very 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 been effectively frozen out by reason of Boltzmann's theorem.

## 5. The spectroscopic behaviour of crystals

In his paper of 1907, Einstein emphasised the intimate relationship indicated by his theory between the thermal properties of crystals and their optical behaviour. It is appropriate therefore that we make a reference here to the decisive support given to the results of the theory set forth above by the experimental facts regarding the spectroscopic behaviour of crystals revealed by investigations made with a great variety of materials and by diverse techniques of investigation. We need not however dilate on this topic, since the experimental situation in this respect has been reviewed in my Lindau address, and since, moreover, the particular case of the diamond which illustrates the general principles in a very striking fashion has been dealt with in detail in a recent lecture published in these *Proceedings*.

## 6. Summary

In Einstein's atomistic approach to the specific heat problem, a crystal is regarded as an assembly of sets of individual harmonic oscillators, each set consisting of a great number of oscillators having a common frequency of vibration. In the present paper, this view is developed and an expression is obtained for the thermal energy of the crystal which appears as a summation of  $(24p - 3)$  terms arising from the individual monochromatic frequencies of internal vibration of the dynamic units of the crystal structure each containing  $8p$  atoms, with a supplementary term which takes account of the translational movements of the same units manifesting themselves as a continuous spectrum of frequencies of vibration within the crystal.