The specific heats of crystals—Part III. Analysis of the experimental data

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1. Introduction

A theory of the specific heats of crystals has been put forward in part I of this series of papers which is based on the determination and enumeration of the normal modes and frequencies of vibration of the atoms in the crystal about their positions of equilibrium. The theory enables the thermal energy of a crystal to be expressed as a function of the temperature in terms of these frequencies. Diamond is admirably suited for a test of the theory, since the frequencies of vibration of the atoms in its structure may be evaluated theoretically and the same frequencies also admit of precise measurement by several different spectroscopic techniques. The specific heat of diamond can accordingly be determined in terms of these frequencies over the whole range of temperatures for which reliable data are available. As has been shown in part II of this series of papers, the theory emerges triumphantly from the test, its results being in complete accord with the results of the spectroscopic investigations on the one hand and with the measured specific heat data on the other.

In the present memoir we shall consider the converse problem of deducing the nature of the atomic vibration spectrum for a given crystal from the empirically determined specific heat data. The method adopted for this purpose may be briefly stated here. We assume that all the atomic oscillators in the crystal have a common frequency of vibration and calculate from the observed specific heat at any given temperature what that frequency is. The frequency thus evaluated itself appears as a function of the temperature, and a graph showing its variation over the entire range of temperature gives us a useful indication of how the total number of degrees of atomic freedom is distributed over the entire range of frequencies covered by the atomic vibration spectrum of the crystal. The results obtained by this procedure and their significance are best understood by considering an actual example. We shall apply the method to the analysis of the specific heat data for diamond and show how useful conclusions may be derived therefrom.
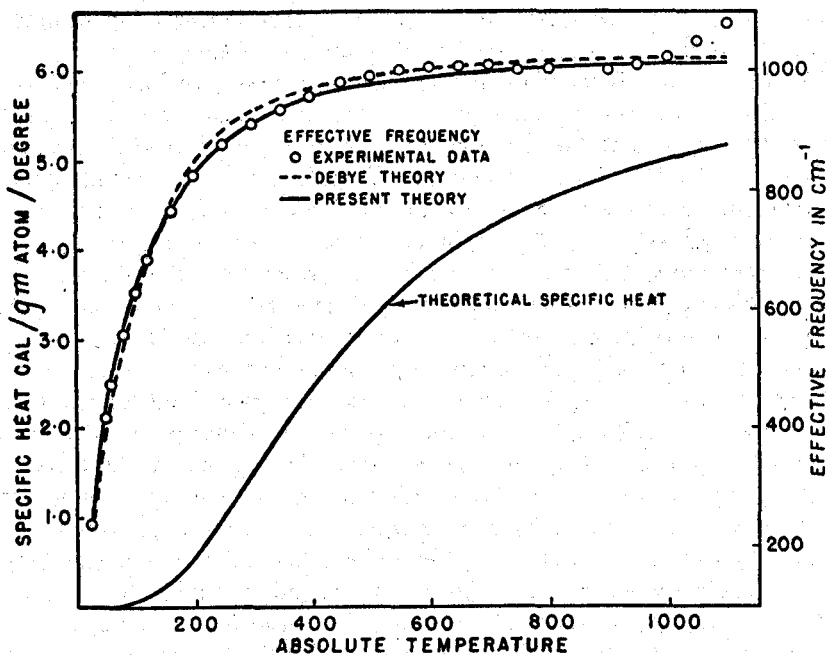
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Figure 1. Analysis of the specific heat of diamond.

2. Analysis of the specific heat curve

In figure 1 above, we reproduce the graph of the specific heat of diamond as a function of the temperature deduced from the spectroscopic data in part II of the present series of papers. The abscissae in the figure are the absolute temperatures, while the ordinates give the calculated specific heats, the scale for the same appearing on the left-hand side of the figure. Taking the value of the specific heat given by this graph for any given temperature and with the aid of a table of Einstein's specific heat function, a frequency of vibration is found which, if ascribed to all the atomic oscillators in the crystal, would give that value for the specific heat at that temperature. We may call the frequency thus evaluated the *effective average* of the atomic vibration frequencies at that temperature. A graph showing how this effective frequency varies with the absolute temperature appears in figure 1 as a continuous curve; the scale of frequencies is that shown on the right-hand side of the figure. It will be seen that the graph is practically a horizontal line at the highest temperatures, the frequency having the value $1016 \, cm^{-1}$ at $1100°$; it then drops very slowly, being 1013 at $1000°$, 1006 at $800°$, and 992 at $600°$ K. Thereafter, it falls a little more quickly, being 978 at $500°$, 954

at 400°, 911 at 300°, 826 at 200° and 767 at 160°. At still lower temperatures, the frequency drops down steeply and at 25° reaches the value 247 cm^{-1}.

The course taken by the frequency-temperature curve is readily understood if we recall the features exhibited by Einstein's specific heat function for various values of the argument; the function vanishes for large values of the argument, while for small values it reaches a limit in the vicinity of which the function does not vary appreciably with the argument; intermediately, however, the function decreases progressively as the argument increases and at an approximately uniform rate. The specific heat curve which we have analysed was obtained by the summation of a set of Einstein functions with different arguments, giving them fractional weights proportionate to the number of oscillators having the particular frequencies. In these circumstances, the "effective average frequency" deduced in the manner explained would necessarily vary with the temperature; at high temperatures, the "*effective average frequency*" would be the same as the *arithmetical average of the frequencies multiplied by their respective weights* but with the very lowest frequencies excluded in casting the average. At moderately high temperatures, the effective average would continue to approximate to the arithmetical average, but if the temperature be so low that the Einstein functions for some of the higher frequencies become vanishingly small, it would show a marked fall and finally, when all the higher frequencies have dropped out in the summation, it is the few surviving oscillators with the lowest frequencies that would determine the effective average frequency. The latter would then be necessarily very small.

The specific heat curve appearing in figure 1 was derived from a set of Einstein functions representing monochromatic frequencies whose values and respective degeneracies are the following: 1332(3), 1250(8), 1239(6), 1149(4), 1088(6), 1008(4), 740(6) and 621(8) and, in addition, a residual continuous spectrum with a weight three. The arithmetical sum of all these vibration frequencies multiplied by their respective degeneracies and divided by the total of 48 is 987 cm^{-1}. If, however, we omit the continuous spectrum and take the arithmetical average after division by 45, we obtain 1022 cm^{-1} as the arithmetical average frequency. This is nearly the same as the value of the effective average frequency at 1100° which is 1016 cm^{-1}. The course of the graph in the middle ranges of temperature is determined by the relative weights of the different frequencies. It will be noticed that these weights are distributed in a more or less uniform manner over the entire range from 1332 cm^{-1} to 621 cm^{-1}. It is this feature which is responsible for the graph of the effective frequency dropping quite gradually from 978 cm^{-1} to 767 cm^{-1} in the temperature range between 500° and 160°.

3. Comparison with the observations

As has already been shown in part II of this series of papers, a highly satisfactory agreement emerges when the specific heat computed from the spectroscopic data

is compared with the values measured by DeSorbo in the temperature range from 40° to 300° and by Magnus and Hodler between 300° K and 1100° K. The same comparison may be made in a different manner, viz., by calculating from the observed specific heat at any temperature the effective average of the frequencies of the atomic oscillators and plotting them on the same graph as the effective average calculated from the theoretical specific heat curve. This has been done and the experimental values are shown as circles in figure 1. The specific heats from 40° to 300° were in the present instance taken from the table of smoothed means given by DeSorbo as best representing his determinations [*J. Chem. Phys.,* 21 876 (1953)]. The experimental data from 300° upwards were those determined by Magnus and Hodler [*Annalen der Physik,* 80 808 (1926)]. It will be seen that over the whole range of temperatures upto 400° the experimental values fall smoothly on the theoretical curve. Between 400° and 1000° the experimental values lie about the theoretical curve, but there are appreciable deviations of about $\pm$ 10 cm^{-1}. In this region of temperatures, this would correspond to variation in the specific heats of about 2 per cent of the measured values. These differences may be reasonably explained as due to inevitable errors in the determination of the specific heats at such high temperatures with small quantities of the material (10 grams).

4. Analysis of Debye's specific heat function

The values for the specific heat of diamond given by Debye's theory have been analysed in the same manner as that explained above and represented in figure 1 as a broken line. In making this calculation, the upper limit of frequency in the Debye integral has been taken to be 1332 cm^{-1} which is the spectroscopically observed highest fundamental frequency. This limiting frequency also fits the experimentally observed specific heats between 450° and 1100° with an accuracy of 1 per cent, the deviations being as often positive as negative. It should also be remarked that the limiting frequency calculated from the elastic constants of diamond comes out as 1304 cm^{-1} in fair agreement with the spectroscopic value of 1332 cm^{-1}.

Comparing now the continuous curve and the broken line appearing in figure 1, it will be seen that the latter lies entirely above the former in the temperature range from 1100° to 140°. The broken curve crosses the continuous curve at about 140° and lies below the latter down to the lowest temperatures.

This difference in the course of the two curves is highly significant. For, it indicates that between 140° and 400°, the Debye theory gives consistently lower specific heats than those actually observed, while between 40° and 140°, it gives higher specific heats than those observed. The actual specific heats, theoretical as well as those observed in these ranges, have been plotted in figures 2 and 3, as continuous and broken curves and as circles respectively, and exhibit this situation very clearly.
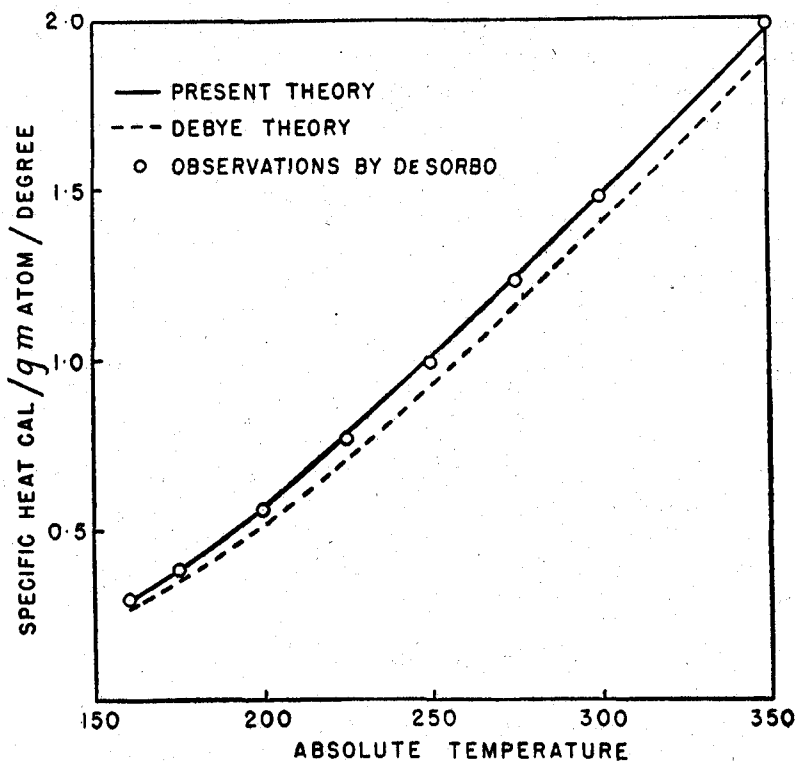
Figure 2. Specific heats of diamond.

5. Comments on Debye's theory

We shall now consider the theoretical implications which attach to the facts elicited by the foregoing analysis.

In the first place we remark that since the effective average frequency in the temperature range between 1100° and 500° lies close to 1000 cm^{-1}, any assumption whatever regarding the distribution of frequencies in the atomic vibration spectrum which gives us 1000 cm^{-1} as the effective average would fit the specific heat data satisfactorily within the limits of error of the experimental determinations. If, for example, we assume that all the atomic oscillators had a frequency of 1000 cm^{-1}, the calculated specific heat would agree with the observed values in that temperature range within one or two per cent. Likewise, if we assume that half the atomic oscillators have a frequency of 1332 cm^{-1} and the other half have the frequency 666 cm^{-1} thereby giving us an average frequency of 999 cm^{-1}, the specific heat data would also be fitted in that range with the same measure of accuracy. It follows that the agreement between the specific heat
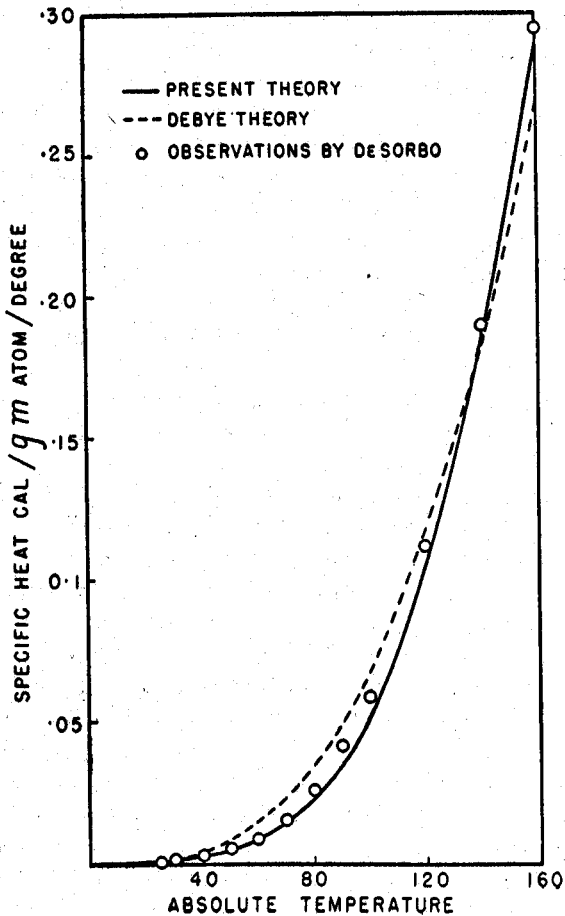
Figure 3. Specific heats of diamond.

theory of Debye and the experimental determinations in this temperature range only indicates that the distribution of frequencies assumed in that theory gives the arithmetical average of the frequencies more or less correctly. That is so, since the arithmetical average is three-fourths of the limiting frequency and is therefore 999 cm^{-1}.

The second remark we have to make is that the precise course of the specific heat curve in the middle range of temperatures, in other words, between 140° and 500°, is of the highest importance in enabling us to decide whether or not any assumed distribution of frequencies agrees with or differs radically from the actual distribution. It has already been remarked that in this range the Debye function gives systematically a lower specific heat than that observed, the

maximum deviation expressed as a percentage being about 10 per cent at about
200° K. The present analysis makes it clear that this difference arises because the
distribution of the frequencies contemplated in the Debye theory differs radically
from the actual distribution; instead of all the frequencies being densely crowded
together near the upper end of the frequency range, they are actually distributed
in a more or less uniform manner over a wide range of frequencies. It may be
remarked that a deviation in the opposite sense, viz., with the calculated values
higher than the observed ones, appears in the same temperature range if we
assume that half the oscillators have a frequency of $1332 \, \text{cm}^{-1}$ and the other half
a frequency of $666 \, \text{cm}^{-1}$. This makes it clear that the actual distribution of
frequencies does not involve a division of the atomic oscillators into two groups
with such widely separated frequencies.

   The third and the final remark that we have to make is in respect of the specific
heats of diamond in the lowest part of the temperature range. The failure of the
Debye theory to represent the course of the specific heat curve in this region is
very conspicuous. A great many measurements were made by DeSorbo in this
part of the temperature range and as he himself has pointed out, they deviate
markedly from the course of the Debye function based on a constant limiting
frequency. DeSorbo has exhibited this failure by drawing a graph representing
the "characteristic Debye temperature" as a function of the temperature, and this
exhibits a pronounced peak at 60°. As will be seen from our figure 3, the specific
heat at this temperature given by the Debye theory assuming the limiting
frequency to be $1332 \, \text{cm}^{-1}$ is 60 per cent in excess of the observed value.

   Debye claimed in his original paper that the explanation of the behaviour of
the specific heat of crystals at the lowest temperatures constituted the major
success of his theory. Since, as we have seen, the theory actually fails most
completely at these same low temperatures in the case of diamond, the only
possible inference which can be drawn from the facts is that the identification of
the thermal energy of crystals with the energy of stationary elastic vibrations in
their interior on which the theory is based is a misconceived idea, in other words,
that the theory itself is fundamentally untenable.

6. Summary

The functional dependence of the specific heat of a crystal on the temperature
may with advantage be expressed as a variation with temperature of the effective
average frequency of the atomic oscillators, the same being determined from the
argument of the Einstein function which gives the observed specific heat at that
temperature. The usefulness of this representation is shown in the paper by a
detailed discussion of the experimental data for diamond. It emerges that the
distribution of frequencies adopted in the Debye theory is irreconcilable with the
observed course of the frequency-temperature curve. It is also pointed out that

the large excess which the specific heat calculated from that theory exhibits over the observed values in the region of low temperatures shows that the ideas on which that theory is based are misconceived and that the theory itself is untenable.