

The specific heats of some metallic elements— Part I. Analysis of the experimental data

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1. Introduction

It is proposed in this paper to analyze the data for the variation of the specific heat with temperature of some metallic elements. The method of analysis is that already explained and discussed in an earlier paper¹ in these *Proceedings* with reference to the specific heat data for diamond, viz., to determine, with the aid of a table of Einstein's specific heat function, the particular frequency of vibration which if assumed to be common to all the atomic oscillators would give for the specific heat of the substance the actual value observed at any given temperature. The frequency thus calculated is designated as the effective average frequency of the atomic oscillators for that substance at that particular temperature. It is itself a function of the temperature and a graph showing how it varies as we proceed from the highest to the lowest temperatures gives useful indications regarding the distribution of the atomic degrees of freedom of motion over the entire range of frequencies in the vibration spectrum.

The four metallic elements the data for which will be analyzed in this paper are aluminium, copper, silver and lead. They all crystallize in the cubic system in forms based on the so-called face-centred cubic lattice which is really a simple Bravais lattice with only one set of equivalent atoms occupying the corners of a rhombohedral unit cell. We shall make use of the data for the specific heats of these metals determined by Giaque and collaborators.² The four metals form a sequence in which the fall of the specific heat at constant volume from the maximum given by the Dulong-Petit formula manifests itself progressively at lower and lower temperatures. There is a special appropriateness in their choice for the present study, since it was the data for these four metals as well as the data for diamond determined by Nernst and Lindmann³ which were made use of by Debye⁴ in a well known paper as support for his theory of the specific heats of crystals.

2. The specific heat data

The specific heat data we make use of are plotted as the lower of the two graphs appearing in figures 1, 2, 3 and 4 which refer respectively to the four metals aluminium, copper, silver and lead. The absolute temperatures are entered on the scale of abscissae at the foot of each figure. The scale of ordinates for the specific heats in cal./gm atom/degree appears on the left-hand side of each figure. The specific heats observed are shown as dotted circles and fall on a smooth curve which touches the axis of abscissae at the lowest temperatures and tends to

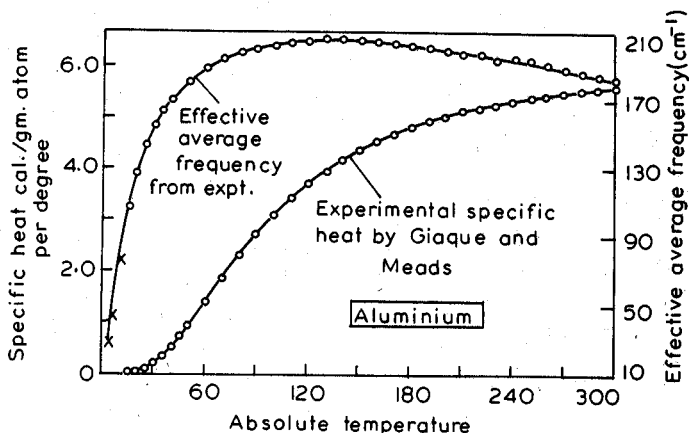


Figure 1. Analysis of the specific heat of aluminium.

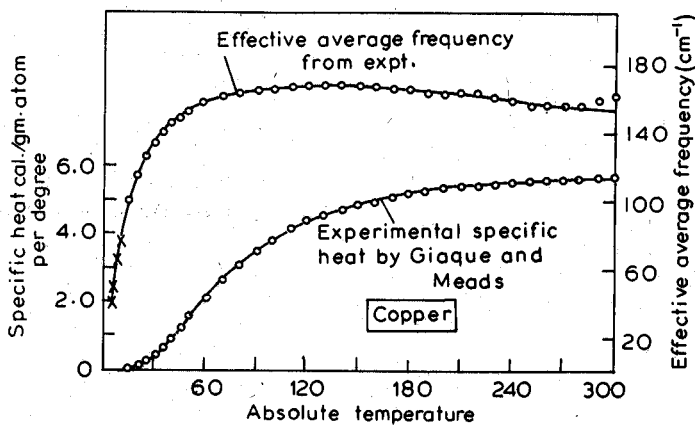


Figure 2. Analysis of the specific heat of copper.

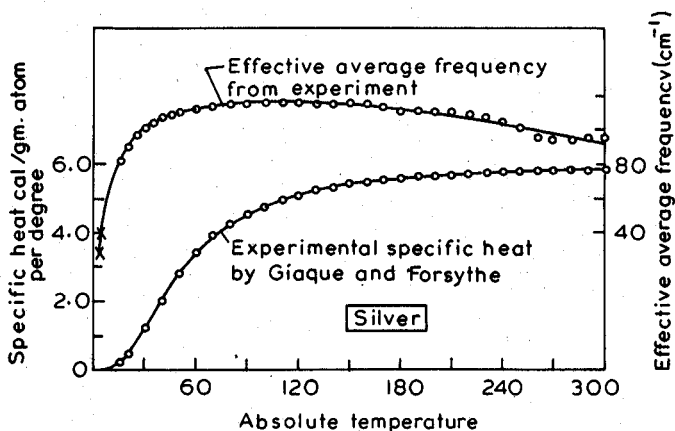


Figure 3. Analysis of the specific heat of silver.

approach the maximum limit at higher temperatures. The scale of ordinates used for the specific heats is rather too small for the values at the very lowest to be adequately represented. The slope of the specific heat curve at the upper end of the temperature range is greatest for aluminium, less for copper, still less for silver, while for lead it is almost indistinguishable from a horizontal straight line.

3. The effective average frequency

The upper of the two graphs in each of the four figures represents the average effective frequency of the atomic oscillators calculated in the manner already explained. The frequencies are shown in the usual spectroscopic nomenclature as wave-numbers and the scale of ordinates for the same appears on the right-hand side of each figure. The calculated values are shown as dotted circles and a smooth curve has been drawn through them. It will be seen that they exhibit a certain amount of scatter in the higher parts of the temperature range in each case. This is not surprising, since a very small error in the determination of the specific heat at this part of the range would represent a large error in the calculation of the effective average frequency. The graphs have been drawn as smooth curves to represent the general trend of the calculated values, ignoring the accidental fluctuations.

It appeared important to continue the graphs to still lower temperatures than those covered by determinations by Giaque and collaborators. Accordingly, we have made use of the data obtained by other authors⁵⁻⁷ for determining the effective average frequency of the atomic oscillators in this lowest part of the temperature range. The computed frequencies are shown as crosses on the

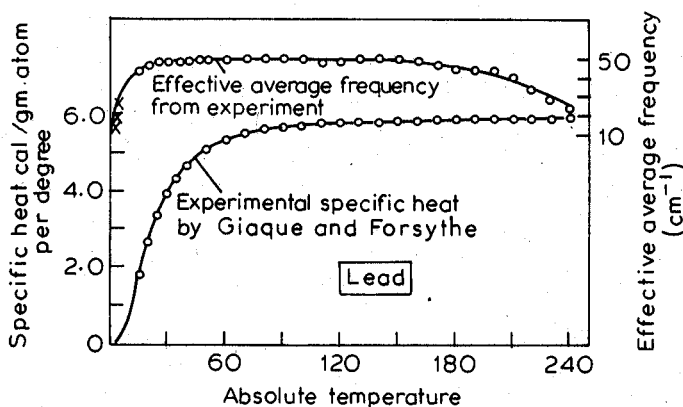


Figure 4. Analysis of the specific heat of lead.

extreme left-hand side of the figure in each case and the graphs have been prolonged so as to pass smoothly through those points.

4. The significance of the results

On a comparison of the frequency-temperature graphs for the four metals, it will be seen at once that while there are certain general similarities, there is also a progressive change in form as we go down the series. All the four curves show a maximum in the middle part of the temperature range covered by the data. This maximum can be located pretty definitely at about 135° K for aluminium. In the case of the other three metals, it becomes progressively more difficult to fix upon a definite temperature as the location of the maximum, the graph being practically a horizontal straight line over an increasingly larger range of temperatures. In other words, the effective average frequency of the oscillators has a practically constant value over a wide range of temperatures. This frequency (in wave-numbers) is 206 for aluminium, 167 for copper, 113 for silver and 50 for lead.

The shape of the graph at low temperatures recalls the course of the graph in the case of diamond already described and discussed in detail in the earlier paper already cited. It is sufficient here to remark that the progressively steeper fall of the graph to low frequencies with the fall of temperature is a consequence of the contribution to the specific heat made by the atomic vibrations of higher frequencies dropping out progressively, until finally at the lowest temperatures we are left only with the contribution made by the vibrations of the very lowest frequencies.

The horizontal stretch of the curves in the middle parts of the temperature range is very clearly analogous to that appearing in the case of diamond throughout the higher parts of the temperature range. Hence, as in the case of

diamond, we infer that in this region the effective average frequency of the atomic oscillators is the same or nearly the same as the arithmetical average of the atomic vibration frequencies, the latter term having the same significance as in the discussion of the data for diamond.

5. Frequency changes at the higher temperatures

We turn next to consider the course of the curve in the higher parts of the temperature range. We may reject any interpretation of the features which it exhibits as arising from errors in experimental data. For, the same phenomenon is shown by all the four metals in the same temperature range but to different extents, as is to be expected. Hence, the only possible interpretation of the drop in the effective average frequency at the higher temperatures shown by the graphs is that the atomic vibration frequencies are themselves a function of the temperature and progressively diminish as the temperature rises. It is not possible from the specific heat data to infer what the rate of such diminution is in the lower parts of the temperature range. But we can definitely infer from the form of the curves at the higher temperatures that the fall of the atomic vibration frequencies with rising temperature is at first rather slow, but that it accelerates and finally reaches a fairly steady rate at the higher temperatures.

The detailed discussion of the effects thus brought to light by our present analysis is more appropriately dealt with in part II of the present paper which concerns itself with the theoretical evaluation of the specific heats of metals as a function of temperature. We may, however, briefly record here some numerical results regarding the rate of fall of the atomic vibration frequencies (expressed as a fraction thereof per degree centigrade) which may be deduced from the slope of the graphs in the case of these four metals. As already remarked, this temperature coefficient is not a constant and we have therefore to consider its value in the vicinity of some temperature at which the graph has a fairly uniform slope. The values deduced in this way are given below in round figures, and represent the quantity $(1/\nu)(\Delta\nu/\Delta T)$, ν being the effective average frequency of the atomic oscillators. The figures for copper, silver and lead indicate a rather steep increase in the temperature coefficients of the atomic vibration frequencies with increasing atomic mass.

Substance	Atomic weight	Temperature	Temperature coefficient of frequency
Aluminium	27.0	255° K	10×10^{-4} per degree
Copper	63.6	250° K	6×10^{-4} "
Silver	107.9	270° K	21×10^{-4} "
Lead	207.2	215° K	99×10^{-4} "

6. Summary

The specific heat data in the temperature range from 15° to 300° reported by Giaque and collaborators for the four metals aluminium, copper, silver and lead are analysed and the effective average frequency of the atomic oscillators deduced therefrom is plotted as a function of the temperature. The graphs exhibit a steep fall of the effective frequency at very low temperatures as is to be expected. In the middle part of the temperature range, the frequency exhibits a broad maximum which in spectral wave-numbers is respectively 206, 167, 113 and 50 for the four metals. At higher temperatures the graph exhibits a second fall which indicates that there is a real and progressive diminution of the actual vibration frequencies of the atoms in the crystal with rising temperature in this range. The effect becomes increasingly more pronounced with increasing atomic mass.

References

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