

The specific heats of some metallic elements—Part III. The characteristic frequencies

SIR C V RAMAN

Memoir No. 93 from the Raman Research Institute, Bangalore

Received February 9, 1957

1. Introduction

In part I of the present series of papers, the experimental data for the specific heat at constant volume of the four metals aluminium, copper, silver and lead were analysed and discussed. The method of analysis was a determination, with the aid of a table of Einstein's specific heat function, of the frequency of atomic vibration which, if assumed to be common to all the atomic oscillators, would give for the specific heat of the solid its observed value at any given temperature. The frequency thus determined is termed the effective average frequency of the atomic oscillators and is itself a function of the temperature. When this is represented as a graph, it discloses a progressive diminution of the frequency in the upper part of the temperature range covered by the data. Considered in relation to the atomic vibration frequencies themselves, this diminution is least conspicuous in the case of *copper*, while the three other metals aluminium, silver and lead form a sequence in which it exhibits an increasing magnitude.

The explanation of these results is not far to seek. The Einstein formula for the energy of an atomic oscillator as function of its frequency and the expression for the specific heat deduced therefrom by differentiation rest on the assumption that the oscillators are *harmonic*. This assumption is however not strictly justifiable. The expansion of volume which all the metals exhibit with rise of temperature can only be understood if we recognize that the atomic oscillators which are the carriers of the thermal energy are anharmonic in their modes of vibration. Such anharmonicity implies that the vibration frequencies of a quantised oscillator do not form a harmonic sequence but that the successive increments of frequency fall off in a regular progression. Simultaneously also, the dimensions of the oscillator would exhibit a progressive increase which is connected with the magnitude of the vibration and its anharmonicity and hence also with the changes of frequency in a quantitative fashion. It is worthy of remark in this connection that the volume expansion between 0° and 300° absolute in the case of the four metals under consideration is least for *copper*, being 1%, while the three other metals,

aluminium, silver and lead form a sequence in which it progressively increases, being 1.2%, 1.3% and 2.2% respectively for these metals. Thus, there is a clear correlation between the rate of thermal expansion and the rate of change of the atomic vibration frequencies which these metals exhibit at higher temperatures as deduced from their specific heat data.

As is well known, the thermal expansion coefficient of a metal tends to zero at the lowest temperatures and at higher temperatures increases *pari passu* with the specific heat. It follows from these facts and the remarks made above that the specific heats of these metals can be adequately represented by a summation of the Einstein functions for frequencies assumed to be independent of the temperature only over the limited part of the temperature range where the overall expansion of the solid is small and may be ignored without sensible error.

In part II of the present series of papers, the characteristic frequencies for the four metals were evaluated by an approximate method based on their relationship to their elastic constants. As was remarked in that paper, the specific heats thus calculated showed distinct deviations from the observed values in the steeply falling part of the curve where its course is specially sensitive to the values chosen for the frequencies. The need for a more precise evaluation was thereby rendered evident. In the present paper, it will be shown that this revision may be effected by making use of the specific heat data themselves in the lower part of the temperature range.

2. The characteristic frequencies

Table 1 below gives the four characteristic frequencies for the four metals calculated approximately from their elastic constants and used in part II. In the adjacent columns are shown the revised values adopted in the present paper. The latter have been determined by trial so as to give the best possible fit with the actual course of the specific heat curve in the lower part of the temperature range in each case. Multiplying each frequency by its degeneracy and dividing the sum total by 21, we obtain the average frequency of the atomic oscillators and this is also shown at the foot of each column.

On an examination of the figures in table 1, it will be seen that in all the four cases, the frequencies as now revised exhibit certain general features in common. Their magnitudes follow each other in the order I, III, II and IV. This is also the order to be expected theoretically, for the cubic spacings are smaller than the octahedral ones and hence should correspond to higher frequencies of vibration, while the longitudinal oscillations in each case should have a notably higher frequency than the transverse ones. Comparing the frequencies determined from the specific heat data with the approximate values estimated from the elastic constants, we also notice certain general features: the frequency of mode I as now deduced is slightly smaller in all the cases; the frequency of mode II is slightly

Table 1. Characteristic frequencies in cm^{-1}

| Mode | Degeneracy | Aluminium | | Copper | | Silver | | Lead | |
|---------|------------|------------------------|---------------------|------------------------|---------------------|------------------------|---------------------|------------------------|---------------------|
| | | From elastic constants | From specific heats |
| I | 3 | 353 | 340 | 260 | 250 | 179 | 179 | 88 | 80 |
| II | 6 | 177 | 200 | 177 | 185 | 109 | 125 | 48 | 45 |
| III | 4 | 287 | 290 | 269 | 215 | 179 | 155 | 87 | 80 |
| IV | 8 | 145 | 160 | 113 | 120 | 70 | 80 | 30 | 34 |
| Average | | 211 | 222 | 182 | 175 | 117 | 121 | 54 | 53 |

larger in all the cases except lead; the frequency of mode IV is distinctly larger in all the four cases, while the frequency of mode III is notably diminished in all the cases except aluminium. These alterations have resulted in an increase by a few per cent of the average of the frequencies for aluminium and silver and a diminution by a few per cent of the average in the cases of copper and lead. They have also resulted in bringing the four frequencies for each metal into the proper relationships with each other to be expected in physical grounds, already remarked.

3. The evaluation of the specific heats

Using the values of the characteristic frequencies now adopted, the specific heat for each of the four metals has been calculated by summing up the Einstein functions for the four frequencies and adding the contribution from the continuous spectrum, the upper limit of frequency for the latter being the same as the lowest of the four characteristic frequencies. From the specific heats thus evaluated, the effective average frequencies of the atomic oscillators have also been evaluated as a function of temperature. In figures 1, 2, 3 and 4, these calculations have been represented graphically. The abscissae in the graphs are the absolute temperatures, while the ordinates for the specific heats and for the effective average frequencies appear respectively on the left- and right-hand sides of the figure. It will be seen that the effective average frequency at the upper end of the temperature range is practically the same as the arithmetical average frequency shown at the foot of the columns in table 1 in each case.

The experimentally determined values of the specific heat and the effective average frequencies calculated therefrom have also been shown in the graphs

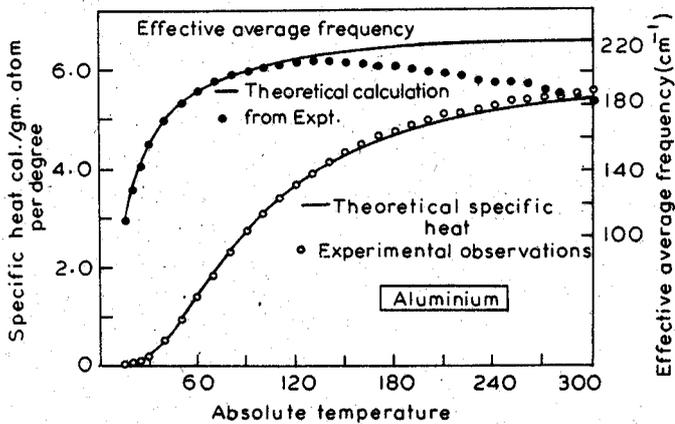


Figure 1. Specific heats of aluminium.

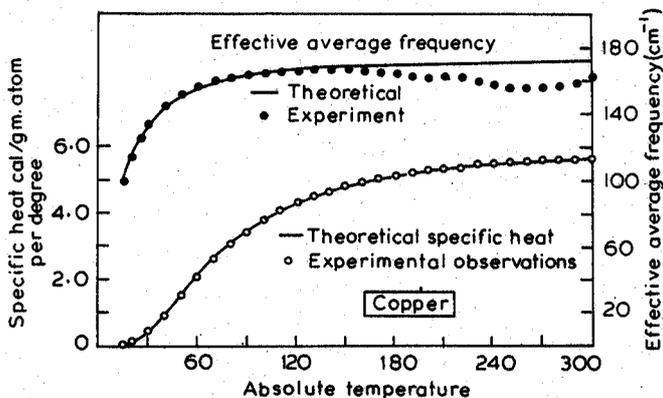


Figure 2. Specific heats of copper.

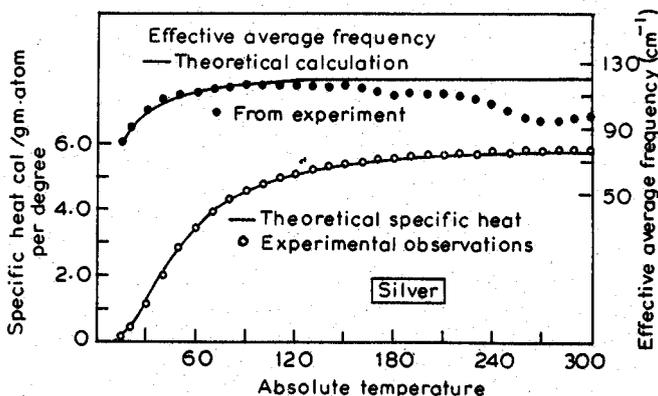


Figure 3. Specific heats of silver.

alongside of the theoretically computed curves in figures 1, 2, 3 and 4. As already stated, the characteristic frequencies employed for the calculation were so chosen as to give the best possible fit with the specific heats in the lower part of the temperature range, i.e., between 15° and 150° absolute in each case. It will be seen that in this part of the temperature range, the observed values fall close to the theoretical curves. On the other hand, in the upper part of the temperature range, i.e., between 150° and 300° absolute, the specific heats observed are consistently higher than the calculated values. The reason for this is evident from the plots of the effective average frequency of atomic vibration. In all the four cases, the atomic vibration frequencies actually effective in the upper part of the temperature range are no longer those deduced from the specific heats at low

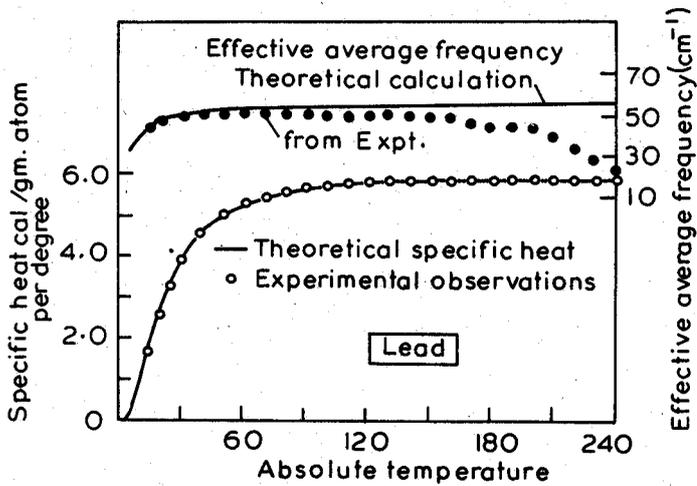


Figure 4. Specific heats of lead.

temperatures but show a progressive diminution with rise of temperature, for the reasons already explained in the Introduction.

Summary

The specific heat data themselves enable us to evaluate more precisely the four characteristic frequencies of each metal determined approximately in part II from their elastic constants. Making use of the new values, the complete specific heat curve is theoretically deduced and shows good agreement with the observations in the lower part of the temperature range, but deviates observably in its upper part, as is to be expected in view of the progressive fall in the frequency of the atomic oscillators with rise of temperature indicated by the analysis of the data in part I. This diminution of the frequencies is a consequence of the anharmonicity of the oscillators which also results in the thermal expansion of the metal. Copper, aluminium, silver and lead form a sequence in the order of increasing coefficients of thermal expansion as also in the magnitude of the temperature coefficients of atomic vibration frequency indicated by their specific heat data.