

The specific heats of some metallic elements—Part IV. The residual spectrum

SIR C V RAMAN

Memoir No. 93 from the Raman Research Institute, Bangalore-6

Received February 25, 1957

1. Introduction

The theory of the specific heats of crystals developed in a recent paper by the present author is based on the result that the structure of a crystal containing p atoms in each unit cell has $(24p - 3)$ normal modes of vibration characterised by sharply defined monochromatic frequencies. These may be described as the modes of internal vibration of the groups of $8p$ atoms each included in volume elements of the crystal whose dimensions are twice as large in each direction as those of the unit cell. The three degrees of freedom of atomic movement left out in this description represent the three translations of each group of $8p$ atoms. The vibration spectrum resulting from these translations may be designated as "the residual spectrum" and its nature was discussed in the paper already cited. The contribution to the thermal energy of the crystal arising from the translations of each group of $8p$ atoms is represented by an integral in which Einstein's expression for the average energy of an oscillator of frequency ν appears multiplied by a quantity $9 \cdot \nu^2 d\nu/\nu^3$ and the product is integrated between the limits 0 and ν_i . The upper limit is the upper limit of frequency in the residual spectrum and is also the lowest of the $(24p - 3)$ frequencies characteristic of the structure.

In the case of the metallic elements now under consideration, $p = 1$ and the residual spectrum thus represents only 3 out of every 24 degrees of atomic freedom of movement. It nevertheless plays a major role in determining the magnitude of the specific heat of the metals at very low temperatures. Hence, a comparison of the experimental data at such low temperatures with the calculated values is of importance for establishing the correctness of the present approach to the theory of their specific heats. It is the object of the present paper to present the results of such a comparison.

As the determinations by Giaque and his collaborators which have so far been the basis of our discussion stop at 15° K, we have necessarily to make use of the results reported by other investigators for still lower temperatures. The

circumstance that the specific heats at such temperatures are very low and increase rapidly with rise of temperature sets a limit to the possible accuracy of their experimental determinations. The specific heat also varies enormously from metal to metal and hence even a small percentage of impurity would affect the determined values, raising them or lowering them, as the case may be. These factors may be responsible for the divergences noticed between the results reported by Giaque and collaborators and those obtained by other investigators in the temperature ranges common to them. These divergences are particularly large in the case of aluminium which has a very low specific heat in the range 0 to 15° K but are less serious in the case of the other three metals, copper, silver and lead.

2. The electronic specific heats

The observed variation of the specific heats of metals with temperature in the vicinity of the absolute zero differs in its features from that observed in the case of insulators, e.g., diamond or the alkali halides. The curves do not touch the axis of the abscissae but meet it at the origin making a definite angle with it. The specific heats in this region can be represented by an expression of the form $AT + BT^3$. These facts are explained on the basis that the first term represents the contribution arising from the thermal agitation of the electrons and the second from the thermal agitation of the atoms themselves. This interpretation finds support in the fact that in the case of metals exhibiting superconductivity, e.g., aluminium and lead, the coefficient A exhibits a distinctly larger value in the range of superconductivity, while the coefficient B remains unaltered.

Table 1. Specific heats at low temperatures
 $C_v = AT + BT^3$

Substance	Range of measurement	$A \times 10^4$	$B \times 10^5$	Auhtor
Aluminium	0-20° K	3.48	0.63	Kok & Keesom
	0- 4° K	3.42	0.68	Howling <i>et al</i>
Copper	0-20° K	1.78	1.24	Kok & Keesom
	0- 5° K	1.64	1.14	Corak <i>et al</i>
Silver	0- 5° K	1.46	4.06	Corak <i>et al</i>
Lead	0- 5° K	7.48	52.04	Horowitz <i>et al</i>

Table 1 shows the results for the four metals now under consideration reported by various authors. It will be seen that the coefficient A is largest for lead; aluminium stands next and is followed by copper and silver, the coefficients for

the latter not being very different. The value quoted in the case of lead is for the state of the metal in which the superconductivity has been eliminated by a strong magnetic field.

It follows from what has been stated above that for a comparison of the experimental data with the results of the present theory, it is necessary to add to the specific heat a term representing the electronic contribution. This has been done, making use of the results of the authors quoted in the table. We shall discuss first the results thus obtained in the case of copper, silver and lead, since in the cases of these metals the determinations which we make use of are in reasonable agreement with those reported by Giaque and collaborators. The case of aluminium where this is not the case will also be discussed.

3. Comparison of theory and experiment

Copper—The specific heat of copper in the range between 0° and 20° K has been reported by Kok and Keesom, while in the more limited range from 0 to 5° K measurements have been made by Corak, Garfunkel, Satterthwaite and Wexler.

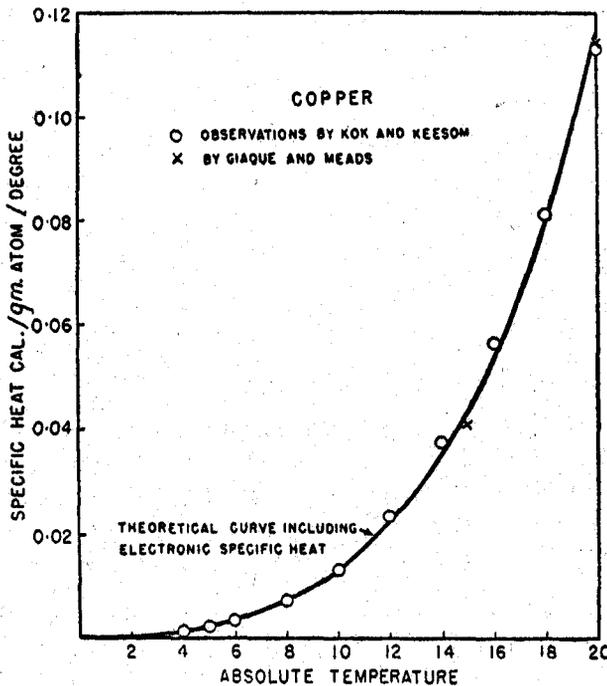


Figure 1. Specific heats of copper.

We present the comparison between theory and experiment in the form of two graphs, one in the range 0 to 20° K and the other in the range 0 to 5° K. In the latter range the results of Kok and Keesom are systematically in excess of those reported by Corak *et al*, the difference being about 8% at 5° K. However, a satisfactory overall agreement between theory and experiment is exhibited by both the graphs.

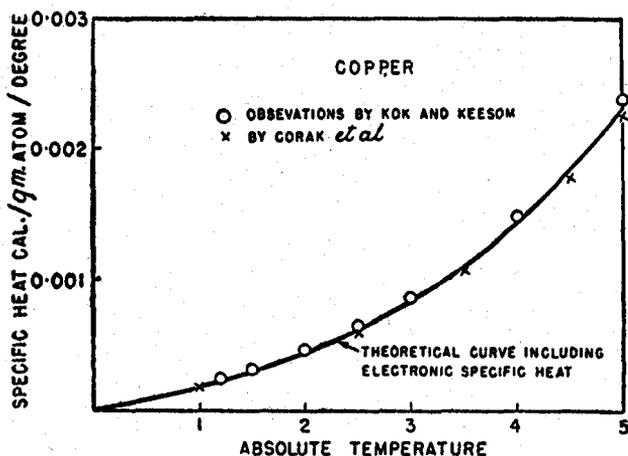


Figure 2. Specific heats of copper.

Silver—Likewise in the case of silver we present the results in the form of two graphs, figures 3 and 4 respectively. Here again, a satisfactory agreement emerges between the theoretical results and the experimental data.

Lead—All the four characteristic frequencies besides the residual spectrum contribute to the observed specific heat at 20° K and this continues to be the case upto 10° K. At still lower temperatures the contributions of only the lowest of the four characteristic frequencies and the residual spectrum predominate. Below 5° K, only the residual spectrum is of importance. As in the previous cases we present a comparison between theory and experiment in the form of two graphs covering the ranges 0 to 20° K and 0 to 5° K as figures 5 and 6 respectively. In figure 5 the available determinations of various authors have all been plotted and it will be seen that between 15° and 20° K the determinations agree generally with each other and with the course of the theoretical curve. Between 5° and 15° K the only observations are those by Keesom and Van den Ende whose results appear to be rather erratic but nevertheless follow the trend of the theoretical curve fairly well. At the lowest temperatures the results of these same authors are noticeably in excess of those deduced from theory. But as will be seen from figure 6 the observations by Horowitz *et al* are in excellent accord with the calculated values.

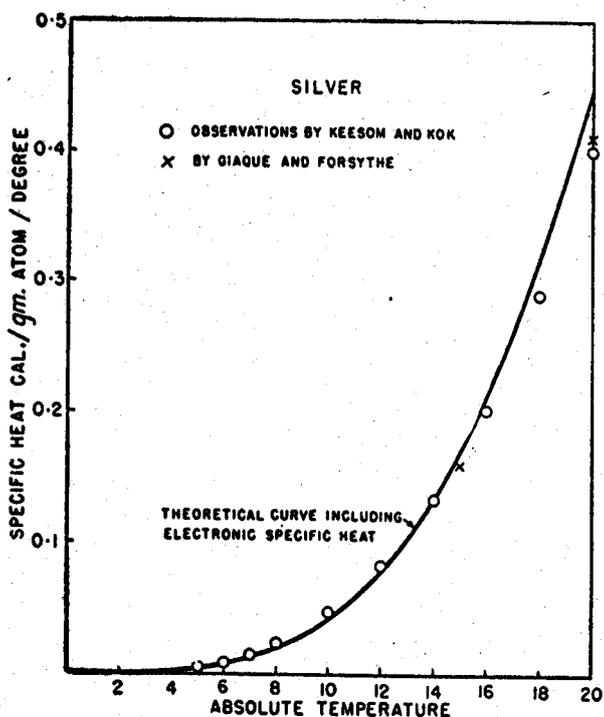


Figure 3. Specific heats of silver.

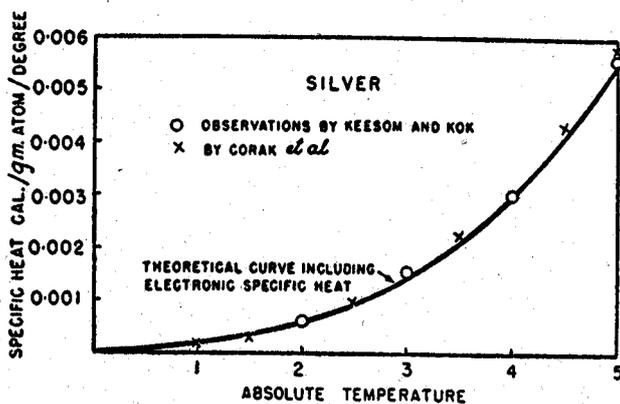


Figure 4. Specific heats of silver.

Aluminium—Of the four metals studied, aluminium has the lowest specific heats in the range 0 to 20° K, and the electronic contribution forms an important part of the whole. Making use of the characteristic frequencies deduced in part III from

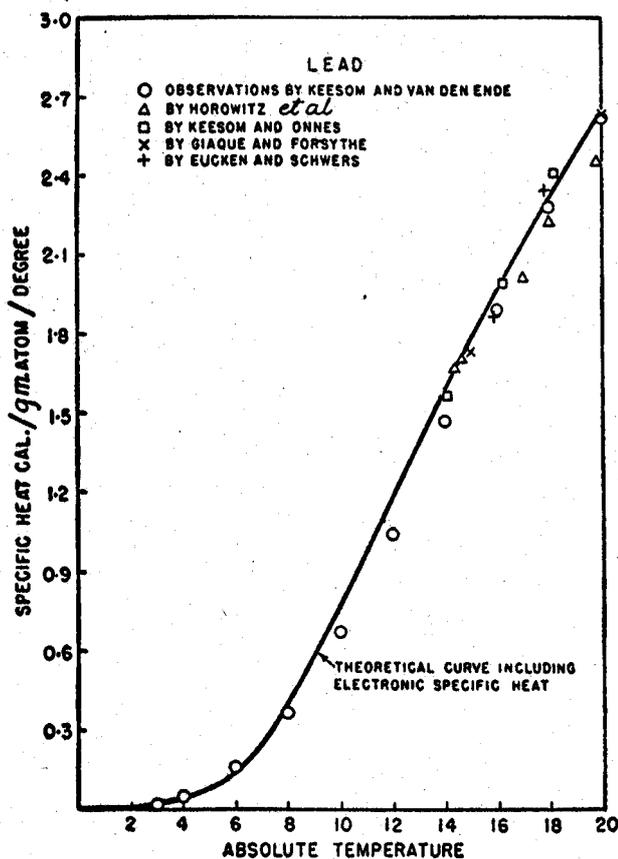


Figure 5. Specific heats of lead.

the specific heat data themselves as reported by Giaque and Meads and taking into account the electronic contribution, the specific heat curve has been computed. The graph thus obtained coincides with the observations reported by Kok and Keesom only at the lowest temperatures where the electronic heat contribution predominates. In the range from 5 to 20° K, the data reported by Kok and Keesom deviate progressively from the theoretical curve, the observed values being everywhere in excess by quantities ranging from 8 to 20% of the calculated ones. They are also in excess of the values reported by Giaque and Meads for 15° and 20° K to a similar extent.

Throughout the range now under discussion the specific heat of aluminium is determined solely by the contribution of the residual spectrum with the addition of the electronic specific heat. The values reported by Kok and Keesom throughout the range would be in fair agreement with the theoretical calculations

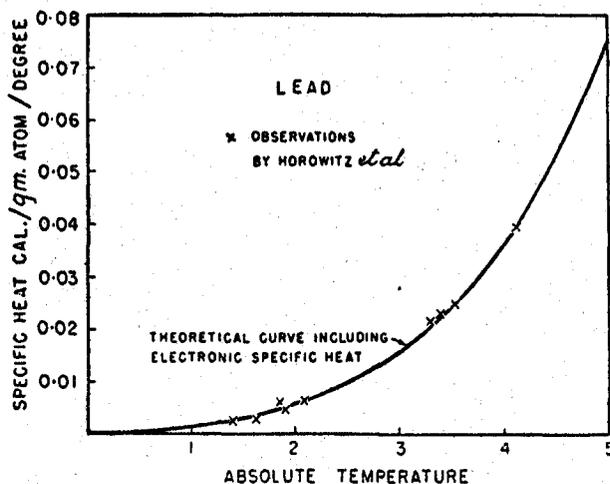


Figure 6. Specific heats of lead.

if the upper limit of frequency in the residual spectrum were taken as 146 cm^{-1} which is nearly the value deduced in part II by an approximate method instead of as 160 cm^{-1} calculated in part III from the specific heat data themselves. But the former assumption would result in the theoretically calculated values at higher temperatures differing from those reported by Giaque and Meads by more than the probable magnitude of their experimental errors. Considering these facts, it appears correct to assume that the values reported by Kok and Keesom for aluminium in the upper part of the temperature range between 0 to 20°K are in excess of the real values by quantities of the order of 10%.

Summary

The theoretical calculation of the specific heats of the four metals aluminium, copper, silver and lead which in part III were shown to be in satisfactory accord with the experimental data reported by Giaque and collaborators in the range from 15 to 300°K have in the present paper been extended down to the absolute zero. When the contribution arising from the thermal agitation from the electrons is included, the calculated specific heats are in satisfactory accord with the results reported by various investigators on the low temperature specific heats of these metals. The agreement is excellent in the cases of copper, silver and lead, but not so satisfactory for aluminium, the available data for which are meagre and appear to be of doubtful accuracy.

References

1. Giaque and Meads *J. Am. Chem. Soc.* **63** 1897 (1941).
2. Giaque and Forsythe *Ibid.* **63** 1902 (1941).
3. Kok and Keesom *Physica* **3** 1035 (Al, Cu) (1936).
4. Corak and others *Phys. Rev.* **98** 1699 (Cu, Ag) (1955).
5. Horowitz and others *Ibid.* **88** 1182 (Pb) (1952).
6. Howling and others *Proc. R. Soc. (London)* **A229** 86 (Al) (1955).
7. Keesom and Kok *Communications Univ. Leiden.* (1932) No. 219(d) and (1933) No. 232(d), (Cu & Ag).
8. Keesom and Van den Ende *Ibid.* (1930) No. 203(d) and (1931), No. 213(c), (Pb).
9. Keesom and Onnes. Eucken and Schwers *Landolt Bornstein Tabellen Hauptwerk* (5 Auflage, 2 Band) p. 1242 (Pb).