The specific heats of some metallic elements—Part II. Approximate theoretical evaluation

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1. Introduction

In this second paper of the series, we consider the problem of evaluating the specific heats of the four metals aluminium, copper, silver and lead, making use of the theoretical ideas set forth in an earlier paper in these *Proceedings*.[1] The metallic atoms in all these four cases are located at the equivalent points of a simple Bravais lattice of which the unit cell is a rhombohedron. Accordingly, all the normal modes of vibration are of the second kind, namely, those in which the successive atoms along one, two or all the three axes of the lattice oscillate with equal amplitudes but with opposite phases. By simple inspection of a model of the structure, it can be seen that the twenty-one possible normal modes of this kind group themselves into only four distinct modes with 3, 6, 4 and 8 as their respective degeneracies. These may be described in simple geometric terms: oscillations of the atoms in the cubic planes along the normals to those planes (degeneracy 3); oscillations of the atoms in the cubic planes tangential to those planes (degeneracy 6); oscillations of the atoms in the octahedral planes normal to those planes (degeneracy 4); oscillations of the atoms in the octahedral planes tangential to those planes (degeneracy 8). Accordingly, the specific heat of these metals is obtained by a summation of the Einstein functions for the frequencies of these four modes multiplied by their respective degeneracies. To this must be added the contribution arising from the spectrum of vibrational frequencies with a statistical weight of three arising from the three translations of the unit cell with the 8 atoms at its corners. This contribution appears as an integration of Einstein functions taken over a continuous spectrum of frequencies, the upper limit of frequency in the integration being the lowest of the four characteristic frequencies.

2. Evaluation of the characteristic frequencies

Each of the atoms in a face-centred cubic lattice has twelve nearest neighbours, six second neighbours, twenty-four third neighbours and twelve fourth neigh-

bours. The six constants needed to determine the force on any one atom resulting from the displacement of another atom reduce, by virtue of the symmetry of the structure, to *three* constants in the case of the nearest neighbours, *two* constants for the second neighbours, *four* constants for the third neighbours and so on. Thus, even if only the first three sets of neighbours are considered, the equations of motion of an atom would involve nine force-constants arising from the displacements of the surrounding atoms. In the absence of any knowledge regarding the magnitudes of these nine constants, it is not possible to evaluate the four frequencies which we need to know. In the case of diamond dealt with in an earlier paper in the *Proceedings*, it was possible to proceed on the basis of its known spectroscopic behaviour and to make an independent evaluation of the eight characteristic frequencies of vibration of its structure. It is obvious that a different procedure has to be adopted in the case of the metallic elements.

What we have to ascertain are the frequencies of vibration of the atomic *layers* lying respectively in the cubic and octahedral planes normally or tangentially to themselves. It is evident that the frequencies of such vibration would depend on the integrated effect on any one *layer* of the movements of the neighbouring layers. Various considerations indicate that the force acting on any layer would be determined *principally by the displacements relatively to that layer of the two neighbouring layers lying one on either side of it.* By way of justifying this statement, we remark that the first, second and third neighbours of any one atom are mostly to be found either in the same layer or in the two adjacent layers. For instance, in the cubic layers all the twelve near neighbours, four out of the six second neighbours and sixteen out of the twenty-four third neighbours are to be found thus located. Likewise, in the octahedral layers all the twelve near neighbours, all the six second nearest neighbours and eighteen out of the twenty-four third neighbours are to be found thus located. Hence, the frequencies of oscillation with which we are concerned may *as a first approximation* be evaluated on the basis that the forces on any one layer arise only from the displacements relative to it of the two neighbouring layers, one on either side of it.

For the same reasons as those explained above, the forces which determine the velocities of elastic wave propagation in the cubic and octahedral directions would likewise be determined *as a first approximation* by the displacements relative to any layer of the two neighbouring layers one on either side. Hence, we are in a position to establish simple but approximate relationships between the characteristic frequencies of vibration of the lattice and the velocities of propagation of elastic waves (longitudinal or transverse as the case may be) in the directions normal to the cubic and octahedral planes respectively. This relation may be written as below:

$$\text{Characteristic frequency} = \frac{2}{\pi} \cdot \frac{\text{Velocity of long elastic waves}}{\text{Twice the distance between adjacent layers}}.$$

The correctness of the formula is easily verified by comparison with the case of

a simple linear lattice, viz., a string under tension loaded with identical mass-particles at equidistant intervals.

3. Numerical results

The foregoing approximate relationships between the velocity of propagation of elastic waves along the octahedral and cubic axes and the characteristic frequencies of a face-centred cubic lattice enable us to evaluate the latter for those crystals for which the elastic constants have been determined with precision. The published determinations make use of the three constants C_{11}, C_{12} and C_{44} contemplated in Voigt's theory. The four velocities we are concerned with are the square roots of C_{11}/ρ, C_{44}/ρ

$$(C_{11} + 2C_{12} + 4C_{44})/3\rho \quad \text{and} \quad (C_{11} - C_{12} + C_{44})/3\rho.$$

In the cases of aluminium[2] and copper,[3] the values of C_{11}, C_{12} and C_{44} are available over a wide range of temperatures from the very lowest upwards. They exhibit a progressive diminution with temperature, which at first is slow but accelerates at high temperatures. In the cases of silver[4] and lead,[5] however, determinations of the elastic constants only at room temperatures are available and we shall make use of them.

Table 1. Characteristic frequencies in wave-numbers.

Mode	Degeneracy	Aluminium		Copper		Silver	Lead
I	3	353	340	260	255	179	88
II	6	177	169	177	171	109	48
III	4	287	302	269	263	179	87
IV	8	145	138	113	109	70	30
Average		211	207	182	177	117	54

Table 1 shows the four characteristic frequencies calculated in the manner explained above. In the cases of aluminium and copper, the values are given at absolute zero as also at room temperature, while in the case of silver and lead, only room temperature values are given. Multiplying the frequencies by the degeneracies of the respective modes, then adding up and dividing by 21, we get the arithmetical average of the four frequencies. This is shown at the foot of the table in each case.

As the elastic constants diminish with increasing temperature but not all in the same manner, it is not altogether surprising to find that one of the calculated frequencies for aluminium actually increases instead of diminishing with rise of

temperature. However, both for aluminium and for copper the arithmetical average shows a noticeable fall at room temperature as compared with the value at the absolute zero.

` 4. Calculation of the specific heats

The expression for the thermal energy of the crystal is given by the formula

$$\frac{N}{8}\left\{ \sum_{i=1}^{i=4} \frac{hv_i}{e^{hv_i/kT}-1} + \frac{3}{v_4^3} \int_0^{v_4} \frac{.hv}{e^{hv/kT}-1} 3v^2 dv \right\},$$

where N is the number of lattice cells contained in the volume of the crystal under consideration. Differentiating this with respect to T, we obtain the specific heat of the crystal at any given temperature. In evaluating the same, we make use of the tabulated values of the well-known functions appearing in the expressions.

The values of the specific heat have been plotted as functions of the absolute temperature in the lower of the two graphs in figures 1, 2, 3 and 4 which refer respectively to the four metals. As usual, the abscissae are the absolute temperatures, and the scale of ordinates for the specific heat appears on the left-hand side of the figure in each case. The upper graph in each figure is the effective average frequency determined from the calculated specific heat in the manner already explained in the previous papers. The scale of ordinates for this frequency appears on the right-hand side of the figure in each case and is expressed in wavenumbers.

It will be noticed that at the upper end of the temperature range in each of the four cases, the effective average frequency of the atomic oscillators deduced from the calculated specific heats is respectively 210, 182, 117 and 55 cm^{-1}. It will also
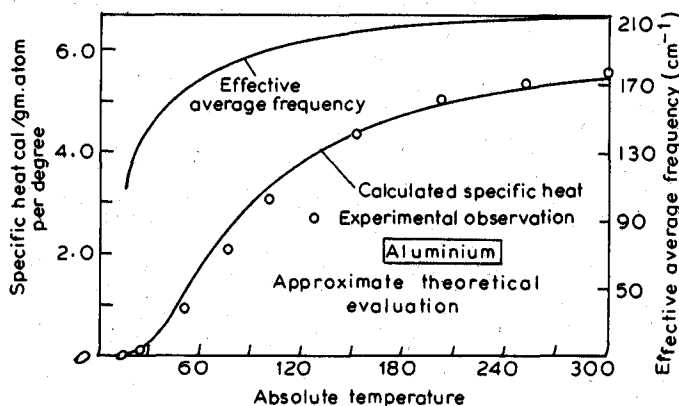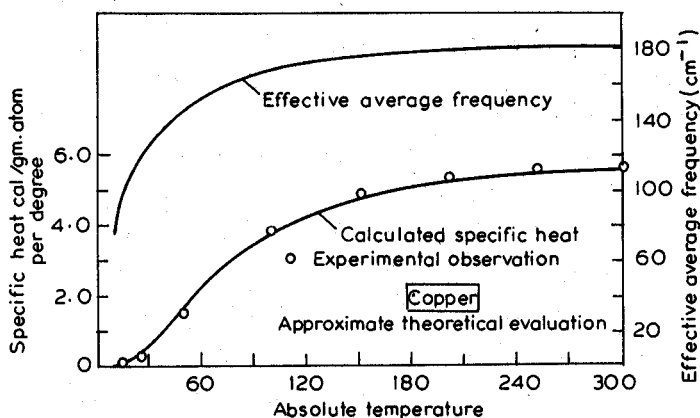

Figure 1. Specific heats of aluminium.

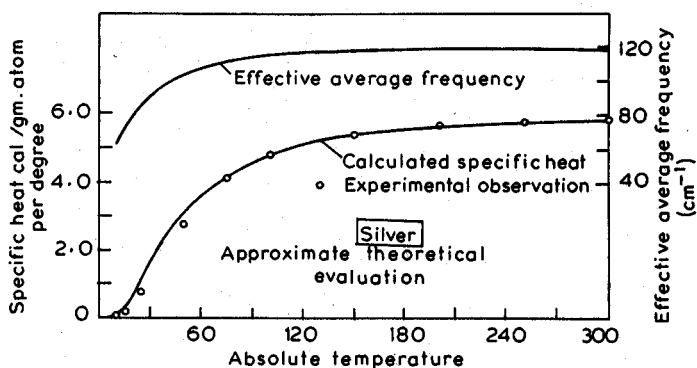**Figure 2.** Specific heats of copper.

Figure 3. Specific heats of silver.

be noticed that these are equal respectively to the arithmetical average of the four characteristic frequencies of each metal shown at the foot of table 1. The effective average frequency falls off quite slowly as the temperature goes down and hence in the upper part of the temperature range, the arithmetical average frequency determines the course of the specific heat curve. Hence any assumption, however arbitrary, regarding the nature of the atomic vibration spectrum would give the specific heat correctly in this part of the range, provided it gives the same arithmetical average for the atomic vibration frequencies. It is only the steeply falling part of the specific heat curve that is sensitive to the precise nature of the assumed vibration spectrum and can furnish reliable information regarding its true complexion.
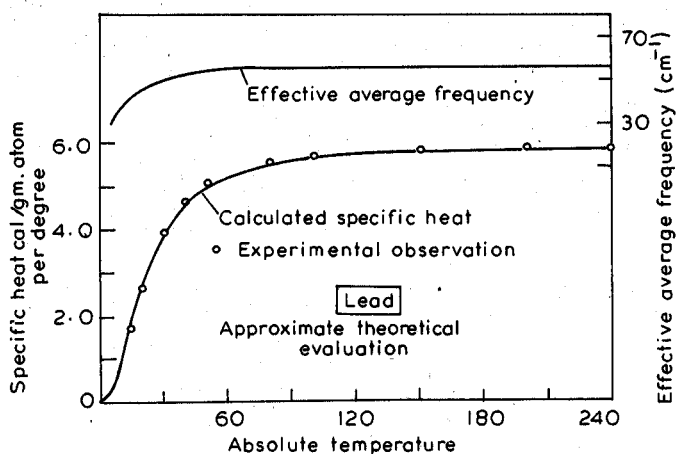
Figure 4. Specific heats of lead.

5. Discussion of the results

In part I of the present series of papers,[6] an analysis of the results of specific heat determinations by Giaque and his collaborators for these four metals was presented and graphs were reproduced showing the effective average frequency as a function of the temperature. These graphs, unlike those appearing in the present paper, do *not* appear as nearly horizontal lines in the upper part of the temperature range in each case, but exhibit a plateau* in the middle part of the range and then slope down to lower values at the upper limit of the range. It is to be inferred from these consequences deduced from the actual specific heat determinations that the atomic vibration frequencies are themselves not independent of the temperature, and that they (or at least their arithmetical averages) diminish progressively as the temperature rises.

The experimentally determined specific heats[7,8] have been plotted alongside of the graphs of the calculated specific heats in figures 1, 2, 3 and 4 of the present paper. In view of the remarks made above, it is to be expected that the observed specific heats would lie above the calculated ones in the upper part of the temperature range. It will be noticed from the figures that this is actually the case. The deviations are fairly conspicuous in the case of aluminium and copper, but are less conspicuous in the cases of silver and lead. The characteristic frequencies for aluminium and copper were calculated from the low-temperature elastic constants, while for silver and lead the frequencies were calculated from the

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*The plateau frequencies are 206, 167, 113 and 50 cm⁻¹ respectively for aluminium, copper, silver and lead. These are somewhat smaller than the arithmetical average frequencies, as is to be expected.

elastic constants at room temperature. The closer approximation actually found between the observed and the calculated specific heats for silver and lead at the higher temperatures is therefore to be expected.

Having regard to the method used for evaluating the four characteristic frequencies, and remembering also that in the present theory we have totally disregarded the anharmonicity of the atomic oscillators, the general agreement between theory and observation over the entire range of temperatures exhibited by figures 1 to 4 may be considered satisfactory. However, it is to be remarked that the observed specific heats are sensibly lower than the calculated ones in the range of temperatures where the specific heat curve slopes steeply down. This is noticeable in the cases of all the four metals and indicates that the characteristic frequencies as determined by the present approximate method need revision. We shall return to this in the third paper of the series.

6. Summary

The specific heats of the four metals aluminium, copper, silver and lead which crystallise as face-centred cubic lattices are evaluated in terms of the four characteristic frequencies of vibration of such a lattice, these latter being determined by an approximate method which relates them to the elastic constants of the crystal. The results thus derived are discussed and compared with the experimentally determined specific heats.

References

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