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# Heat Capacity of Aluminum between 2.7 and 20°K*

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The heat capacity of aluminum has been measured between 2.7 and 20°K, and the results are in quantitative agreement with results derived from inelastic neutron scattering experiments. There is an initial increase of $\Theta_D$ at low temperatures which cannot be accounted for in terms of the elastic constants.

## INTRODUCTION

At low temperatures heat-capacity measurements provide a direct comparison with thermodynamic properties derived from inelastic-neutron-scattering experiments. Gilat and Nicklow[1] have made a detailed analysis of phonon-dispersion curves of aluminum obtained from the neutron-scattering measurements of Stedman and Nilsson,[2] and Yarnell *et al.*[3] From this analysis Gilat and Nicklow have calculated the frequency distribution $G(\nu)$, and from $G(\nu)$ calculated the Debye temperature $\Theta_D$ as a function of temperature. An interesting result of their analysis is an initial increase in $\Theta_D$ at low temperatures.

Existing heat-capacity measurements[4] on aluminum in the range 4–20°K are not sufficiently precise to compare with values derived from the neutron-scattering analysis. Phillips[5] has measured the heat capacity of aluminum from 0.1 to 4°K and has deduced the value of $\gamma$, the coefficient of the electronic contribution to the heat capacity, and the value of $\Theta_0^c$, the limiting value of $\Theta_D$ as $T$ approaches zero. Dixon *et al.*,[6] have also made measurements in the region below 4°, however their values of $\gamma$ and $\Theta_0^c$ are somewhat higher than the values derived by Phillips. Giauque and Meads[7] have made heat-capacity measurements from 300° down to 15°K. This paper reports the results of heat-capacity measurements in the region of 2.5 to 20°K. The results show that neutron and thermodynamic measurements are in quantitative agreement when the experiments are carried out at low temperatures where anharmonic effects are small.

## CALORIMETRIC SAMPLE

The calorimetric sample was taken from a large polycrystalline ingot kindly given by F. W. Young, Jr. of this laboratory. The ingot had been initially purchased from United Mineral and Chemical Corporation, New York, and was stated to be 99.9999% pure material. Spectrographic analysis showed this not to be the case. The analytical results are shown in Table I. As seen from Table I the purity is more nearly 99.99%.

The ingot was cut into cubes $\frac{1}{4}$ inch on a side. The pieces were then cleaned, heavily etched, and vacuum annealed ($1\times10^{-5}$ Torr) at 500°C for two hours. The grain size was 1–3 mm. The cubes were loaded into the calorimeter vessel and the vessel evacuated to $1\times10^{-6}$ Torr. The vessel was then sealed with $2.8\times10^{-6}$ mole of helium inside to serve as an exchange gas. There was no trouble with adsorption of the helium at the lowest temperatures. The time for thermal equilibrium to be established after addition of heat to the calorimeter and

TABLE I. Analysis of aluminum sample (ppm).

| | | | |
|---|---|---|---|
| Ag | <1 | Fe | 5 |
| B | 4 | Mg | 3.0 |
| Ba | 10 | Mn | 0.2 |
| Ca | 40 | Na | 3 |
| Cr | 2 | Ni | <0.3 |
| Cu | 0.4 | Si | 10 |

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[1] G. Gilat and R. M. Nicklow, Phys. Rev. **143**, 487 (1966).

[2] R. Stedman and G. Nilsson, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965) Vol. I, p. 211.

[3] J. L. Yarnell, J. L. Warren, and S. H. Koenig, in *Lattice Dynamics, Proceedings of the International Conference Held at Copenhagen*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1963), p. 57.

[4] J. A. Kok and W. H. Keesom, Physica **4**, 835 (1937).

[5] N. E. Phillips, Phys. Rev. **114**, 676 (1959).

[6] M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. Roy. Soc. (London) **A285**, 561 (1965).

[7] W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941).

TABLE II. Experimental values of the heat capacity $C_p$ in units of $j/g$ at. deg.

| $T$ | $C_p$ | $\Theta_D$ | $T$ | $C_p$ | $\Theta_D$ |
|---|---|---|---|---|---|
| 2.770 | 0.004264 | 428.8 | 10.400 | 0.04028 | 436.8 |
| 3.248 | 0.005224 | 429.8 | 10.575 | 0.04181 | 437.1 |
| 3.522 | 0.005833 | 428.7 | 11.518 | 0.05104 | 437.4 |
| 3.735 | 0.006322 | 429.3 | 11.574 | 0.05115 | 437.7 |
| 4.008 | 0.006992 | 429.5 | 12.581 | 0.06310 | 437.8 |
| 4.223 | 0.007543 | 429.8 | 12.644 | 0.06391 | 437.8 |
| 4.521 | 0.008366 | 429.8 | 13.609 | 0.07674 | 437.8 |
| 4.702 | 0.008880 | 430.4 | 13.768 | 0.07901 | 437.9 |
| 5.035 | 0.009901 | 430.7 | 14.786 | 0.09481 | 437.9 |
| 5.188 | 0.01040 | 430.6 | 14.581 | 0.09599 | 437.7 |
| 5.570 | 0.01171 | 431.2 | 15.836 | 0.1140 | 436.8 |
| 5.702 | 0.01219 | 431.4 | 15.898 | 0.1152 | 436.7 |
| 6.128 | 0.01383 | 431.8 | 16.815 | 0.1343 | 435.8 |
| 6.234 | 0.01426 | 431.8 | 16.923 | 0.1369 | 435.6 |
| 6.694 | 0.01623 | 432.6 | 17.763 | 0.1571 | 434.2 |
| 6.770 | 0.01658 | 432.7 | 17.926 | 0.1614 | 433.7 |
| 7.488 | 0.02015 | 433.2 | 18.702 | 0.1826 | 432.3 |
| 7.532 | 0.02038 | 433.3 | 18.915 | 0.1892 | 431.6 |
| 8.457 | 0.02572 | 434.8 | 19.753 | 0.2153 | 429.9 |
| 8.536 | 0.02623 | 434.8 | 19.952 | 0.2222 | 429.2 |
| 9.403 | 0.03221 | 435.9 | 20.755 | 0.2514 | 426.9 |
| 9.562 | 0.03341 | 436.0 | 21.024 | 0.2617 | 426.2 |

sample was a few seconds at the lowest temperatures, increasing to 2–3 min near 20°K.

The sample weight was 141.946 g (5.2609 g at.).

## EXPERIMENTAL

The measurements were made in an adiabatic calorimeter similar to that described by Morrison *et al.*[8,9] However, in the present apparatus the Simon bomb has been replaced by a 900 cc liquid-helium container, and the adiabatic shield is automatically controlled.[10]

The calorimeter vessel carried both a capsule-type platinum resistance thermometer and an Allen Bradley 10-Ω, $\frac{1}{2}$-W carbon resistor. The platinum thermometer was calibrated by the National Bureau of Standards on the 1955 Provisional Temperature Scale.[11]

The carbon thermometer was used as the working thermometer and was calibrated for each experiment by direct comparison with the platinum thermometer in the range $11<T<20$°K. Below 4° the carbon thermometer was calibrated on the 1958[12] helium vapor-pressure scale with a helium vapor-pressure thermometer attached to the adiabatic shield. From these fixed points, three were used (20, 14, and 4°K) to determine the constants in the interpolation formula given by Clement and Quinnell.[13]

$$\log_{10}R+(K/\log_{10}R)=A+(B/T).$$

$R$ is the measured resistance at temperature $T$; $K$, $A$, and $B$ are the constants determined from the three fixed points. The shifts in resistance of the carbon thermometer each time it was cooled from room temperature were small, amounting to only a few tenths of an Ω at 4°K. The deviations of the carbon temperature scale from the thermodynamic scale were determined in separate series of experiments with a gas thermometer bulb attached to the calorimeter vessel.

Because space limitations prevented the inclusion of a hydrogen vapor-pressure thermometer, the accuracy of the platinum thermometer calibration at two of the fixed points (20 and 14°K) was obtained indirectly. The refrigerant used to cool the calorimeter assembly to 20°K was equilibrium hydrogen (99.8% para, 0.2% ortho). Helium exchange gas was admitted to the cryostat to bring the calorimeter vessel and shield into thermal contact with the liquid-hydrogen bath. The pressure was then reduced over the liquid hydrogen by means of a large vacuum pump. The pumping rate was such that at least an hour was required to pass through the triple point. During this time the drift rates of the platinum and carbon thermometers were zero and the indicated temperature difference between the calorimeter vessel and adiabatic shield was zero. Passage through the triple point was marked by the sudden onset of a cold drift by the thermometers. The pump was then turned off and the system allowed to warm through the triple point. This procedure gave identical values of the temperature based on the platinum thermometer; however this temperature was 0.01°K higher than the value due to Woolley *et al.*,[14] who obtained 13.803°K, corrected to the N.B.S. 1955 Provisional Scale. Ter Harmsel *et al.*,[15] give 13.802°K as the triple point from their measurements of the heat of vaporization of equilibrium hydrogen.

Next the platinum thermometer was used to calibrate the gas thermometer at 20°K and the comparison was repeated at the equilibrium hydrogen triple point. From two determinations the gas thermometer gave values of $T_{\mathrm{Pt}}$-$T_{\mathrm{gas}}$ equal to 0.008 and 0.011°K. At 4°, temperatures given by the gas thermometer, calibrated at 20°K with the platinum thermometer, agreed to within 0.002°K with temperatures obtained from the helium vapor-pressure thermometer on the adiabatic shield. From these measurements the platinum thermometer cannot be in error by more than 0.008°K at 20°K.

## RESULTS AND ANALYSIS

The primary experimental heat capacities are listed in Table II. $C_p$-$C_v$ corrections are negligible over the temperature range of the measurements. The inaccuracy of the measurements is thought to be no worse than

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[8] J. A. Morrison, D. Patterson, and J. S. Dugdale, Can. J. Chem. **33**, 375 (1955).

[9] W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 467 (1957).

[10] T. M. Gayle and W. T. Berg, Rev. Sci. Instr. **37**, 1740 (1966).

[11] G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Res. Natl. Bur. Std. **57**, 67 (1958).

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[15] H. ter Harmsel, H. van Dijk, and M. Durieux, Physica **33**, 503 (1967).

±2% below 4°K and ±0.5% for $10<T<20$. Between 2.5 and 4°K the present results may be compared with those of Phillips.[5] The largest difference between the two sets of data in this region is 0.3%. At 15°K the present results are 4% higher than those of Giauque and Meads,[7] at 17°—0.9% higher, and at 20°K—9.0% lower.

At low frequencies the lattice frequency spectrum can be expressed as a power series

$$G(\nu)=N(\alpha\nu^2+\beta\nu^4+\mu\nu^6+\cdots)\,, \tag{1}$$

where $N$ is the number of atoms in the crystal. The corresponding expression for the lattice heat capacity is

$$C_L=aT^3+bT^5+cT^7+\cdots\,, \tag{2}$$

where $a$ is related to the Debye temperature at 0°K.

$$\Theta_0{}^c=(1943.7/a)^{1/3}. \tag{3}$$

For metals there is also an electronic contribution to the heat capacity, and simple theory gives this to be proportional to the temperature so that the total heat capacity $C_v$ is given by

$$C_v=\gamma T+C_L. \tag{4}$$

To extract the lattice contribution from the experimental heat capacities the value of $\gamma$ given by Phillips was used ($1.350\times10^{-3} j/g$ at. deg$^2$). The Debye temperatures calculated from the heat capacities after subtracting the electronic part are given in Table II and are plotted as a function of temperature in Fig. 1. The smooth curve in Fig. 1 shows the Debye temperatures calculated from the $G(\nu)$ obtained form the analysis of the inelastic neutron-scattering data. The smooth curve of Fig. 1 is slightly different from the curve given in Fig. 3 of Ref. 1. This is because $G(\nu)$ has been recalculated[16,17] with the object of obtaining increased accuracy at low frequencies.

The experimental heat capacities below 13°K with the $\gamma$ value of Phillips were used to derive by a least-squares analysis[17] the coefficients $a$, $b$, and $c$ in Eq. (2). These values $\Theta_0{}^c$ and $\Theta_0$ calculated from the elastic constants,[18] $\Theta_0$ (elastic), are given in Table III. A plot of $(C_v-\gamma T)/T^3$ versus $T^2$ is shown in Fig. 2. The smooth curve is the resulting fit to the experimental results given by the least-squares analysis. Because the electronic heat capacity is over 75% of $C_v$ at 4°, an attempt was made to get an approximate value of $\gamma$. The least-squares analysis was repeated with the variables $\gamma$, $a$, $b$, and $c$ to be determined. The resulting value of $\gamma$ was $1.348\times10^{-3} j/g$ at. deg,[2] in good agreement with Phillips's value of $1.350\times10^{-3}$.

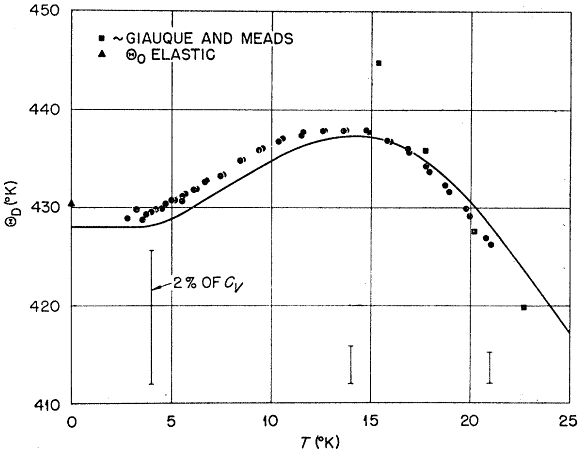

FIG. 1. The Debye temperature plotted as a function of temperature. The vertical bars show the effect of a 2% change in the heat capacity, keeping the electronic contribution constant. The filled circles are the results of the present work. The smooth curve represents results derived from inelastic neutron-scattering experiments (see text).

TABLE III. The coefficients in Eq. (1), $\Theta_0{}^c$ and $\Theta_0$ (elastic).

| | | |
|---|---|---|
| $a$ | ($j/g$ at. deg$^4$) | $(2.483\pm0.015)\times10^{-5}$ |
| $b$ | ($j/g$ at. deg$^6$) | $(-2.10\pm0.20)\times10^{-8}$ |
| $c$ | ($j/g$ at. deg$^8$) | $(6.5\pm1.5)\times10^{-11}$ |
| $\Theta_0{}^c$ | present work | 427.8±1°K |
| $\Theta_0{}^c$ | Phillips[a] | 427.7±1°K |
| $\Theta_0{}^c$ | Dixon *et al.*[b] | 436.4±0.7°K |
| $\Theta_0$ | (elastic)[c] | 430.3°K |

[a] Reference 5. [b] Reference 6. [c] Reference 18.

## DISCUSSION

$\Theta_0{}^c$ derived from the present results is in excellent agreement with the value quoted by Phillips and 2% lower than $\Theta_0{}^c$ given by Dixon *et al.*[6] Agreement of $\Theta_0{}^c$ with $\Theta_0$ (elastic), although outside the uncertainty limits, is within 0.6%. Also, $\Theta_D$ values from the heat-capacity measurements and inelastic neutron-scattering work are in agreement at these low temperatures.

The feature of an initial increase of $\Theta_D$ at low temperatures is the result of the negative value of $b$ in Eqs. (2) and (4) and hence a negative value of $\beta$ in Eq. (1). This type of temperature variation of $\Theta_D$ at low temperatures is somewhat unusual. From a continuum model, Blackman[19] has shown that an initial increase of $\Theta_D$ can arise if certain relations among the elastic constants fulfill rather stringent requirements. Bhatia and Horton[20] in their work on silver have used a model that gives a maximum in $\Theta_D$ at low temperatures by making the proper choice of elastic constants.

The elastic constants of aluminum fall far short of satisfying these requirements. Blackman[21] has pointed out that once the lattice frequencies are sufficiently large so that $G(\nu)$ cannot be described by an elastic continuum, no general rule can be given about the sign of $\beta$.

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[18] G. N. Kamm and G. A. Alers, J. Appl. Phys. **35**, 327 (1964).

[19] M. Blackman, Proc. Roy. Soc. (London) **A164**, 62 (1938).

[20] A. B. Bhatia and G. K. Horton, Phys. Rev. **98**, 1715 (1955).

[21] M. Blackman, Proc. Cambridge Phil. Soc. **33**, 94 (1937).

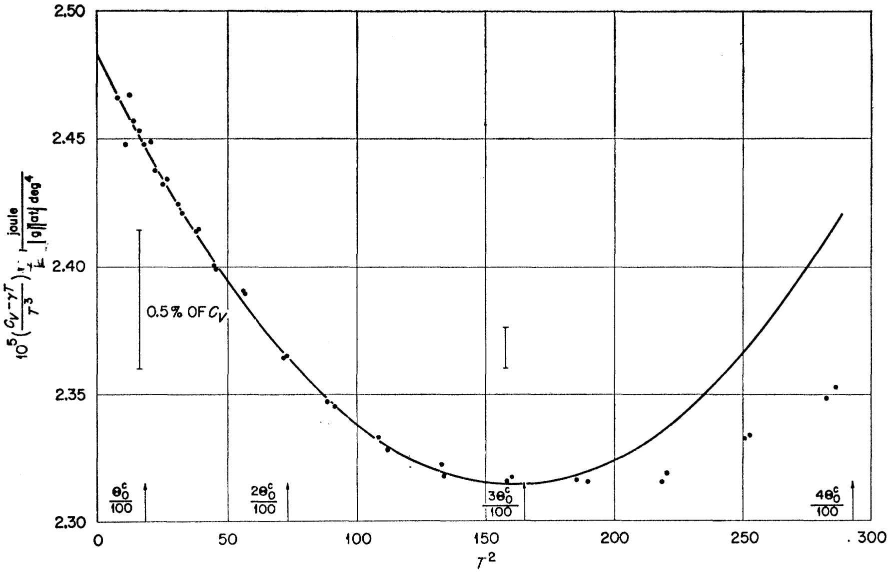

FIG. 2. A plot of $(C_v-\gamma T)/T^3$ versus $T^2$. The smooth curve shows the resulting fit of a least-squares analysis to the experimental points at the lowest temperatures. The vertical bars show the effect of a 0.5% change in the heat capacity, keeping the electronic contribution constant.

The cause of negative $\beta$ is not obvious from the dispersion curves themselves. Dolling[17] has investigated the effect on $\Theta_D$ of replacing that part of $G(\nu)$ from $\nu=0$ to various values of low frequency, $\nu_i$, by a term proportional to $\nu_i^2$. No qualitative changes in the shape of the curve were produced by varying $\nu_i$ from 0.1 to $1\times10^{12}$ cps. The smooth curve in Fig. 1 corresponds to $\nu_i=0.3\times10^{12}$ cps. This indicates that rather high frequencies are important in determining the temperature dependence of $\Theta_D$ at low temperatures.

Martin[22] has measured the heat capacity of gold from 0.4 to 1.5°K and from 3 to 30°K and found the initial temperature dependence of $\Theta_D$ similar to that of aluminum. In this case the elastic constants of gold[23] are much closer to satisfying the conditions of the models used by Blackman and by Bhatia and Horton. As we have seen in the case of aluminum, however, this kind of temperature dependence of $\Theta_D$ can arise from $G(\nu)$ as determined from the precise behavior of the phonon-dispersion curves at relatively high frequencies. This behavior cannot be predicted from a knowledge of the elastic constants alone. If the phonon-dispersion curves could be measured for gold by inelastic neutron-scattering techniques, it would be of interest to carry out an analysis for $G(\nu)$ and $\Theta_D$ similar to that for aluminum. It seems quite possible that the origin of the "anomalous" behavior of $\Theta_D$ of gold at low temperatures is the same as that of aluminum.

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