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Low-Temperature Specific Heat of Antimony*

D. C. McCollum and William A. Taylor
University of California, Riverside, California
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The specific heat of antimony has been measured from 0.54 to 4.0°K. A least-squares fit to the data in the 0.54 to 1.1°K range gave $C=(0.105\pm0.002)T+(0.210\pm0.002)T^3+(0.0048\pm0.0004)T^{-2}$ mJ/mole °K and a Debye temperature of 210.0±0.7°K. The uncertainties are rms deviations of the means. These results are in good agreement with specific-heat, Fermi-surface, and quadrupole-resonance data. Thermometer calibration in the He^3 range is discussed.

INTRODUCTION

The electronic specific heat of antimony is much smaller than that of an ordinary metal, and several different values are to be found in the literature.[1–3] The experiments reported here were undertaken as part of an investigation of semimetals and their alloys, to determine whether or not high-purity materials studied at helium-3 temperatures would yield specific-heat values that were consistent with data from cyclotron-resonance, de Haas–van Alphen, and nuclear-quadrupole-resonance experiments.

EXPERIMENTAL PROCEDURE

A 266-g specimen of antimony having an impurity content of one part per million was obtained from Cominco Products, Inc. A germanium-resistance thermometer was inserted into a hole drilled in the specimen, a small amount of Apiezon J oil in the hole serving to increase the thermal contact between specimen and resistor. A heater consisting of about 1000 Ω of 1.5-mil Formvar-coated manganin wire was wound on the specimen and secured at each end with a drop of GE 7031 varnish which had been thinned with toluene. Heater and thermometer leads were of 5-mil manganin wire. It was assumed that half of the heat developed in the heater leads went to the specimen; this amounted to about 7/10% of the total power supplied to the specimen. The specimen was suspended from cotton threads kept under tension by springs. The heat capacity of the addenda was measured and subtracted from the total observed heat capacity. The measurements were made in a helium-3 cryostat to be described in detail elsewhere.[4] A mechanical thermal switch having indium-coated copper jaws served to cool the specimen from room temperature without the use of exchange gas.

A germanium resistance thermometer having a resistance of about 1000 Ω at 4.2°K was calibrated between 1 and 4.2°K against helium-4 and helium-3 vapor pressures, and was then used for specific-heat measurements in this range. Another germanium resistor having a resistance of about 700 Ω at 1°K was calibrated between 0.5 and 1.1°K against the magnetic susceptibility of chromium-potassium alum. $T-T^*$ for this salt varies approximately linearly from zero to about 5 mdeg in this temperature region.[5] To fit this calibration data an expression of the form

$$1/T=\sum_i A_i(\ln R)^i \qquad (1)$$

was used, then a table of differences between calculated and measured temperatures was compiled and from it a smooth curve of corrections to the above power series was constructed. Three terms in the series were used to fit the resistor used above 1°K. Eight terms were used to fit the resistor used in the lower temperature range, but fewer would have sufficed.

It has been suggested that copper is a suitable standard for use in checking techniques of specific-heat measurement.[6] A specimen of about nine moles of copper containing less than ten parts per million impurities was obtained from Cominco Products, Inc. and its heat capacity was measured using the same resistance thermometers and the same procedures used in the antimony runs. The specific heats of both copper and antimony below 1.1°K showed systematic irregularities of a few percent, which was taken to indicate that the temperature calibration of the germanium resistor should be modified. Accordingly the graph of corrections to the power series (1) for the low-temperature resistor was changed where necessary to make the specific heat of copper smooth and equal to the average of the several results cited by Dixon *et al.*[7] During this process the changes made were less than 5 mdeg. The copper and antimony data taken with the higher temperature resistor was smooth except for a hump in the small region 1.0–1.12°K which was caused by the condensation of the helium exchange gas in the germanium-resistor capsule. Data in this region were not included in the results listed in Table I and shown in

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[2] Norman M. Wolcott, Bull. Am. Phys. Soc. 1, 289 (1956).

[3] Harvey V. Culbert, Bull. Am. Phys. Soc. 10, 1104 (1965).

[4] William A. Taylor, thesis, University of California, Riverside, California (unpublished).

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Fig. 1. Then as an additional check, the specific heat of a 2.7-mole sample of tin containing less than ten parts per million impurities was measured, again using the same resistance thermometers and procedures. Both tin and antimony data were now found to vary smoothly. The tin results were compared to those of O'Neal and Phillips[8] below 1°K and those of Corak and Satterthwaite[9] between 1 and 4°K, and were found to agree within 2% at all temperatures, which is the estimated accuracy of our measurements. The estimated precision, verified by the consistency of results from different runs on the sample, is about 0.5%.

RESULTS AND DISCUSSION

The results of these experiments are given in Table I. Between 0.5 and 1.1°K the specific heat of antimony might be expected to have a temperature dependence given by

$$C=\gamma T+\beta T^3+\alpha T^{-2}, \tag{2}$$

where the first term is due to electrons, the second to lattice vibrations, and the third to the orientation of nuclear quadrupole moments in the electric-field gradient of the lattice and electrons. The specific-heat data indicates that at higher temperatures in the liquid-helium range the lattice term is no longer proportional to T^3. This can be seen in Fig. 1, which is a plot of C/T versus T^2. In the region above 1°K, where the T^{-2} term is negligible, the data would lie on a straight line if the lattice term were proportional to T^3. The quadrupole term is the first term in an expansion in inverse powers of T which would have to be extended at lower temperatures, but in this range the other terms can be shown to be negligible by using data from nuclear-quadrupole-resonance work in antimony.[10] A least-squares fit of 51 data points in the temperature range below 1.1°K was made by minimizing $\sum_i \{(\gamma T_i+\beta T_i^3+\alpha T_i^{-2}-C_i)/C_i\}^2$. The rms deviations of the means were calculated and are given below as the

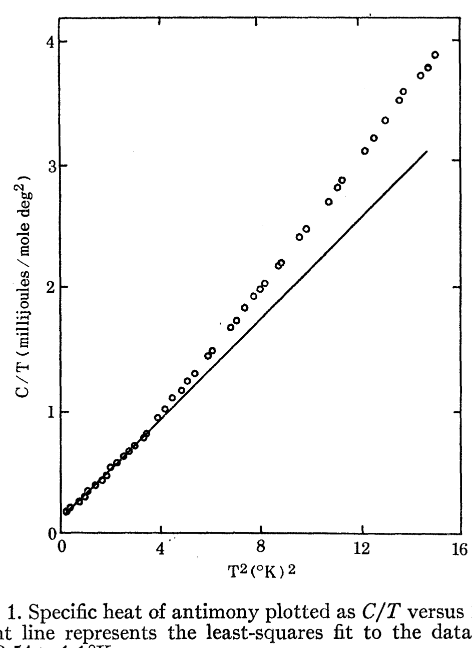

FIG. 1. Specific heat of antimony plotted as C/T versus T^2. The straight line represents the least-squares fit to the data in the range 0.54 to 1.1°K.

TABLE I. Specific heat of antimony.

T(°K)	C (mJ/mole deg^2)	T(°K)	C (mJ/mole deg^2)	T(°K)	C (mJ/mole deg^2)
0.572	0.1146	1.146	0.448	2.417	3.51
0.580	0.1170	1.162	0.466	2.450	3.63
0.586	0.1169	1.170	0.472	2.613	4.44
0.608	0.1234	1.233	0.534	2.640	4.57
0.608	0.1237	1.238	0.538	2.717	5.01
0.615	0.1264	1.248	0.551	2.784	5.39
0.620	0.1286	1.249	0.543	2.805	5.51
0.632	0.1313	1.273	0.577	2.821	5.60
0.647	0.1380	1.280	0.585	2.827	5.67
0.660	0.1406	1.325	0.639	2.837	5.70
0.682	0.1488	1.326	0.642	2.848	5.77
0.688	0.1512	1.333	0.653	2.953	6.44
0.702	0.1568	1.342	0.664	2.966	6.51
0.704	0.1573	1.373	0.713	2.967	6.54
0.707	0.1573	1.405	0.767	3.093	7.39
0.729	0.1656	1.406	0.765	3.099	7.44
0.732	0.1676	1.407	0.767	3.140	7.76
0.732	0.1688	1.441	0.815	3.150	7.83
0.738	0.1702	1.464	0.852	3.271	8.87
0.749	0.1744	1.482	0.883	3.327	9.36
0.755	0.1773	1.484	0.872	3.337	9.46
0.766	0.1816	1.491	0.894	3.352	9.57
0.786	0.1904	1.491	0.896	3.492	10.87
0.799	0.1997	1.509	0.920	3.541	11.33
0.808	0.205	1.570	1.014	3.545	11.43
0.818	0.209	1.571	1.017	3.605	12.06
0.833	0.217	1.572	1.011	3.682	12.87
0.834	0.217	1.576	1.047	3.710	13.25
0.841	0.220	1.623	1.094	3.795	14.12
0.847	0.223	1.661	1.169	3.829	14.46
0.850	0.227	1.680	1.239	3.881	15.09
0.875	0.241	1.695	1.235	4.013	16.91
0.875	0.243	1.723	1.296		
0.890	0.248	1.746	1.338		
0.894	0.249	1.771	1.406		
0.917	0.263	1.788	1.460		
0.919	0.265	1.797	1.445		
0.932	0.275	1.818	1.500		
0.953	0.286	1.849	1.585		
0.960	0.292	1.881	1.665		
0.969	0.299	1.905	1.732		
0.970	0.302	1.930	1.823		
0.972	0.300	1.970	1.901		
0.980	0.305	2.021	2.090		
1.018	0.333	2.029	2.07		
1.021	0.336	2.112	2.38		
1.034	0.345	2.166	2.51		
1.035	0.347	2.198	2.59		
1.053	0.360	2.245	2.80		
1.062	0.365	2.302	2.99		
1.121	0.429	2.325	3.05		

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[9] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

[10] R. R. Hewitt and B. F. Williams, Phys. Rev. **129**, 1188 (1963).

uncertainties of the coefficients:

$$C=(0.105\pm0.002)T+(0.210\pm0.002)T^3+(0.0048\pm0.0004)T^{-2}\ \text{mJ/mole °K}. \quad (3)$$

From Eq. (3), $\gamma=0.105$ mJ/mole °K^2, in agreement with Culbert's value of 0.103 ± 0.004 mJ/mole °K^2.[3] Recent analyses of the Fermi surface of antimony[11,12] indicate that there are three closed electron surfaces and six closed hole surfaces. For purposes of comparison of specific-heat data with de Haas–van Alphen and cyclotron resonance data, these surfaces will be assumed to be ellipsoidal because of the lack of the detailed information which would be needed for calculations based on a nonellipsoidal model. With this simplifying assumption,

$$\gamma=\left(\frac{\pi k^3}{h^3}\right)^{2/3} m_0 V\left\{(m_1'm_2'm_3')^{1/3}\left(\frac{N_e}{V}\right)^{1/3}+(2)^{2/3}(M_1M_2M_3)^{1/3}\left(\frac{N_h}{V}\right)^{1/3}\right\}, \quad (4)$$

where the m_i are the electron effective-mass ratios, the M_i are the hole effective-mass ratios, both referred to the principal-axis system, and N_e/V and N_h/V are the total number of electrons and holes per unit volume, respectively. Windmiller and Priestley[12] find $N_e/V=N_h/V=5.36\times10^{19}$ cm^{-3}. Datars and Vanderkooy[13] give effective-mass ratios of $m_1'=0.068$, $m_2'=0.92$, $m_3'=0.050$, $M_1=0.093$, $M_2=1.14$, $M_3=0.088$. However, Falicov and Lin[11] indicate that the carrier assignment assumed by Datars and Vanderkooy is incorrect. Thus, according to Falicov and Lin, Datars and Vanderkooy's mass ratios should read $m_1'=0.093$, $m_2'=1.14$, $m_3'=0.088$, $M_1=0.068$, $M_2=0.92$, $M_3=0.050$. Using Falicov and Lin's assignment of the carriers, Eq. (4) gives $\gamma=0.103$ mJ/mole °K^2. In view of the assumptions made above it is difficult to estimate just how exact the agreement is between this calculated value and that derived from the specific heat, but it is clear that they are in accord.

The parameter β in Eq. (2) is related to the Debye Θ by $\beta=(12/5)\,\pi^4R(1/\Theta)^3$. From the coefficient of the T^3 term in Eq. (3), $\Theta=210.0\pm0.7$°K, in excellent agreement with Culbert's value of 210.2 ± 1.0°K[3] and somewhat higher than the other two results.[1,2]

The nuclear–specific-heat term in (2) is

$$\frac{\alpha}{T^2}=\frac{R}{80}\frac{(2I+2)(2I+3)}{2I(2I-1)}\left(\frac{e^2qQ}{kT}\right)^2, \quad (5)$$

where I is the nuclear spin. Naturally occurring antimony is 57.25% Sb^{121}, for which $I=\frac{5}{2}$ and 42.75% Sb^{123}, for which $I=\frac{7}{2}$. From the nuclear–quadrupole-resonance measurements of Hewitt and Williams,[10] it follows that e^2qQ/k is equal to 3.69 mdeg for Sb^{121} and to 4.70 mdeg for Sb^{123}. Inserting these numbers into (5) leads to $\alpha=4.37\times10^{-3}$ mJ°K/mole, which agrees with the specific-heat result within the estimated uncertainty.

CONCLUSIONS

There are now two independent measurements of the specific heat of antimony that are in good agreement with each other and with other Fermi-surface data. Results of the measurements reported here are also in agreement with nuclear–quadrupole-resonance data, but extension of the specific-heat measurements to lower temperatures would be necessary for a precise determination of the quadrupole term by this method.

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