PHYSICAL REVIEW VOLUME 134, NUMBER 2A 20 APRIL 1964

Low-Temperature Heat Capacities of Gallium, Cadmium, and Copper*

NORMAN E. PHILLIPS†

Inorganic Materials Research Division of the Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California

(Received 18 November 1963)

The heat capacities of gallium, cadmium, and copper have been measured from 0.1 or 0.2°K to 4.2°K. The experimental data for copper suggest that the measurements are accurate to within 3% at 0.1°K and to within 1% at temperatures above 0.2°K. In the superconducting state both gallium and cadmium show the typical deviations from the BCS law of corresponding states. The nuclear quadrupole contribution to the heat capacity of gallium was observed in the normal state but not in the superconducting state. The absence of this contribution in the superconducting state state can be used to set an approximate lower limit of 60 sec for the spin-lattice relaxation time at 0.25°K. For cadmium $\theta_0=209.0\pm2.3$°K, in reasonable agreement with the value calculated from the elastic constants.

I. INTRODUCTION

THE heat-capacity measurements on gallium and cadmium reported here were originally undertaken to determine the electronic contribution to the heat capacity of the superconducting state. For both these metals the contribution of the lattice to the superconducting-state heat capacity is a relatively small part of the total, and the electronic contribution can therefore be studied at temperatures well below the transition temperature. The heat capacity of cadmium is also of interest for comparison with the elastic constants, and there is a contribution to the heat capacity of gallium associated with the interaction between the nuclear quadrupole moment and electric-field gradients in the crystal.

The heat capacity of a metal is usually taken to be the sum of electronic and lattice contributions. In the normal state the electronic heat capacity is proportional to the temperature, and the normal-state heat capacity C_n is given by

$$C_n=\gamma T+C_l, \tag{1}$$

where γ is a constant, T is the temperature, and C_l is the lattice heat capacity. At low temperatures, C_l can be represented by a power series in T,

$$C_l=AT^3+BT^5+\cdots, \tag{2}$$

and for temperatures below certain limits determined by the coefficients in Eq. (2) C_n is given by

$$C_n=\gamma T+AT^3 \tag{3}$$

or

$$C_n=\gamma T+AT^3+BT^5. \tag{4}$$

Until recently it has been quite generally assumed that the superconducting-state heat capacity C_s is given by

$$C_s=C_{es}+C_l, \tag{5}$$

where C_{es} is the electronic contribution and C_l, the lattice heat capacity, is the same as in the normal state. Heat-capacity measurements on indium[1,2] have been interpreted as showing that C_s becomes less than the value of C_l derived from normal-state measurements, and that one of the above assumptions is therefore incorrect. The final explanation of the indium measurements may involve a change in C_l at the superconducting transition or possibly a modification of the assumption of separate lattice and electronic heat capacities, but we shall continue to use Eq. (5) in the analysis of the experimental data. A change in C_l similar to the one observed in indium would not be significant for the results reported here, and no satisfactory alternative to Eq. (5) has yet been given.

The apparatus used has been described in connection with similar measurements on aluminum[3] and zinc.[4] At temperatures below 0.3°K, these measurements showed the presence of appreciable errors in the heat capacity produced by errors in temperature measurement. The measurements on gallium and cadmium were made shortly after those on aluminum and zinc, and some of the results have been reported briefly.[5] A more complete report has been delayed until the temperature scale used below 0.3°K could be corrected. This has been accomplished as described in the next section, and for the data reported here errors associated with temperature measurement are believed to be less than 1% at temperatures above 0.2°K but as much as 3% at 0.1°K.

---

* This work was supported by the U. S. Atomic Energy Commission.

† Alfred P. Sloan Research Fellow.

[1] C. A. Bryant and P. H. Keesom, Phys. Rev. Letters 4, 460 (1960).

[2] H. R. O'Neal, N. M. Senozan, and N. E. Phillips, *Proceedings of the Eighth International Congress on Low-Temperature Physics, London, 1962* (Butterworths Scientific Publications, Ltd., London, 1962).

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

[4] N. E. Phillips, Phys. Rev. Letters **1**, 363 (1958).

[5] The measurements on cadmium below 1°K were presented at the Thirteenth Annual Calorimetry Conference, Chicago, 1958 (unpublished). The measurements on gallium below 1°K have been reported in *Proceedings of the Eighth International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1961).

II. TEMPERATURE MEASUREMENTS BELOW 1°K: THE HEAT CAPACITY OF COPPER

Temperature measurements below 1°K were based on the magnetic susceptibility of copper potassium sulfate. If the susceptibility of this salt follows the Curie-Weiss law, the mutual inductance of the coils surrounding the salt is a linear function of $(T-\Delta)^{-1}$. The assumed validity of the Curie-Weiss law and a value of $\Delta=0.033$°K provided the basis for temperature measurements below 1°K in the work on zinc and aluminum.[3] Below 0.3°K this led to measured values of C_n/T which were obviously inconsistent with values obtained by extrapolation from higher temperatures: the measured C_n/T was 10% higher than the extrapolated for aluminum at 0.1°K. The fractional discrepancy was approximately the same for both zinc and aluminum, suggesting that the effect was a consequence of errors in the temperature scale for copper potassium sulfate. Measurements on other samples have shown that this is at least partly true. No such discrepancies are observed down to 0.2°K if a value of $\Delta=0.042$°K is used: for a number of samples (including zinc and aluminum in the normal state) with heat capacities that could be predicted from measurements at higher temperatures the measured hear capacity agreed with the predicted to within 1% at temperatures above 0.2°K. Below 0.2°K discrepancies still occur. They are not reproducible but amount to at most 2 or 3% at 0.1°K. Usually the measured heat capacity is less than the expected. These remaining errors appear to be associated with temperature gradients in the salt pill during the calibration of the carbon thermometer: Smaller errors are observed when calibration points are taken after longer times have been allowed for the salt and sample to come to thermal equilibrium and when the steady-state heat leak to the salt is small. When insufficient time for thermal equilibrium is allowed or when the heat leak to the salt is high, the measured temperature is too low, since the interior of the salt pill is colder than the surface to which the sample is attached, and the mutual inductance is determined by an average over the whole pill. The rapid reduction in these effects with increasing temperature is to be expected from the strong temperature dependence of the thermal diffusivity of the salt. In summary, a temperature scale based on the above extrapolation with $\Delta=0.042$°K gives heat-capacity results accurate to about 1% at 0.2°K and 3% or better, depending on the conditions under which the calibration points are taken, down to 0.1°K. All measurements reported here were calculated using this extrapolation below 1°K and the 1958 He^4 scale[6] above 1°K.

One rather direct test of the accuracy of these measurements is provided by a comparison between the heat capacity of an induim sample as measured in this apparatus[7] and the heat capacity of the same sample as measured in an apparatus employing a spherical crystal of cerium magnesium nitrate for the temperature measurements.[2] The two sets of data agree to within 1% above 0.2°K.

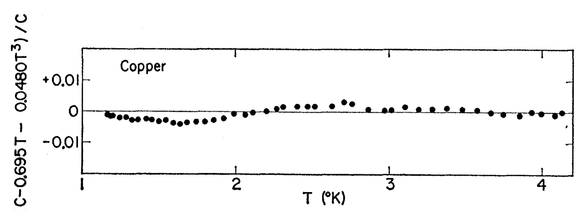

FIG. 1. The heat capacity of copper: measurements in the liquid-helium cryostat.

As a further test of the accuracy of these measurements we have made heat-capacity measurements on a sample of copper and compared them with the heat capacity of the same sample in the liquid-helium temperature region. Copper is particularly useful for such a test because its heat capacity is well known at temperatures above 1°K. Furthermore, a reliable extrapolation of the heat capacity to lower temperatures is possible: the T^5 term in C_l is negligible below 4°K, both γ and A can be measured accurately above 1°K, and there is no reason to expect any contribution to the heat capacity other than the lattice and electronic terms at temperatures near 0.1°K. The data obtained in the liquid-helium cryostat are shown as deviations from Eq. (3) in Fig. 1. The deviations are systematic, but for the most part are less than 0.3%. As shown in Table I the parameters γ and A obtained in this work are in satisfactory agreement with the majority of other recent determinations in the liquid-helium region. The measurements in the adiabatic demagnetization cryostat are shown in Fig. 2 as a plot of C/T versus T^2. The straight line found to fit the measurements above 1°K is shown for comparison. Except for the lowest points, near 0.13°K, the agreement is well within 1%.

TABLE I. Comparison of recent heat-capacity measurements on copper at liquid-helium temperatures.

	γ (mJ mole^{-1} deg^{-2})	A (mJ mole^{-1} deg^{-4})
This work	0.695	0.0480
Corak *et al.*[a]	0.688	0.0478
Rayne[b]	0.686	0.0473
Griffel *et al.*[c]	0.691	0.0486
Ramanathan and Srinivasan[d]	0.720	0.0523
Manchester[e]	0.696	0.0478
duChatenier and deNobel[f]	0.721	0.0500
Kneip[g]	0.698	0.0482

[a] W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **98**, 1699 (1955).

[b] J. A. Rayne, Australian J. Phys. **9**, 189 (1956).

[c] M. Griffel, R. W. Vest, and J. F. Smith, J. Chem. Phys. **27**, 1267 (1957).

[d] K. G. Ramanathan and T. M. Srinivasan, J. Sci. Ind. Res. (India) **16B**, 277 (1957).

[e] F. D. Manchester, Can. J. Phys. **37**, 989 (1959).

[f] F. J. du Chatenier and J. de Nobel, Physica **28**, 181 (1962).

[g] G. Kneip (private communication).

---

[6] E. Brickewedde, H. van Dijk, M. Durieux, J. Clement, and J. Logan, J. Res. Natl. Bur. Std. **64A**, 1 (1960).

[7] H. R. O'Neal and N. E. Phillips (unpublished).

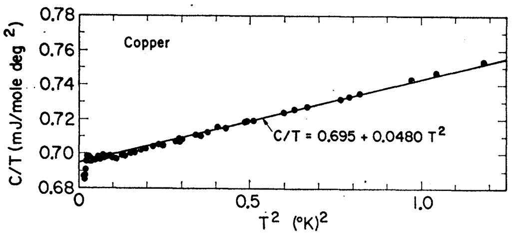

FIG. 2. The heat capacity of copper: measurements in the adiabatic demagnetization cryostat.

III. THE HEAT CAPACITY OF GALLIUM

The heat-capacity measurements were made on a 300 g polycrystalline sample of 99.999% purity. The critical temperature was found to be $T_c = 1.078$°K by observing the change in slope of a warming curve as the sample was warmed through the transition in zero magnetic field. No heat-capacity points with small temperature increments were taken to define the width of the zero-field transition, but as judged from the warming curve the transition was at least 90% complete in an interval of 0.001°K or less. These figures represent limits set by the sensitivity and response time of the thermometer circuit.

Figure 3 shows the points obtained in the adiabatic demagnetization cryostat for both the normal and superconducting states. The data for the two states are discussed separately in the following sections.

A. Normal State

It is evident from Fig. 3 that there is a contribution to C_n that is not included in Eq. (3). This additional contribution is the high-temperature tail of a Schottky anomaly produced by the interaction of the nuclear quadrupole moment with the electric-field gradients in the crystal. The lowest temperatures reached in these experiments are high enough for this contribution to be proportional to T^{-2}, and Eq. (3) can therefore be generalized to represent the gallium data by the addition to the right-hand side of the term $C_q = \alpha T^{-2}$. The coefficients α and γ were determined as the intercept and slope of a straight line fitting the lowest normal-state points on a plot of C_nT^2 versus T^3. Part of this plot is shown in Fig. 4. The coefficients A and B were then obtained by plotting $C_n - \gamma T - \alpha T^{-2}$ versus T^2, as shown in Fig. 5.

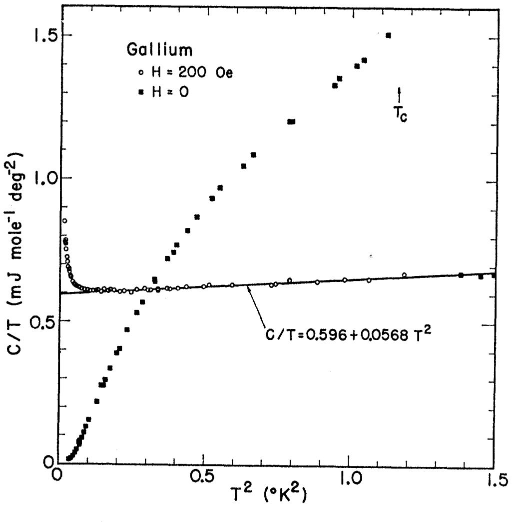

FIG. 3. The heat capacity of gallium: measurements in the adiabatic demagnetization cryostat.

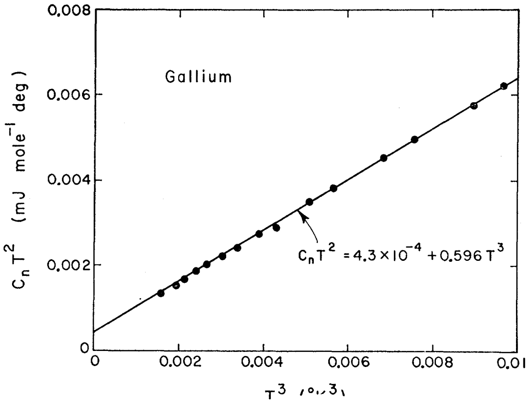

FIG. 4. The normal-state heat capacity of gallium at $T < 0.21$°K.

The Debye characteristic temperature θ_0, defined by

$$A = (12/5)\pi^4 R\theta_0^{-3}, \tag{6}$$

where R is the molar gas constant, is 324.7°K. If the lattice heat capacity is represented by a temperature-dependent Debye θ, defined by equating C_l to the Debye heat-capacity function of T/θ, θ deviates appreciably from θ_0 at unusually low reduced temperatures. The difference amounts to 5% at $\theta_0/100$.

The normal-state parameters are given in Table II together with other experimental data. In this table and in subsequent tables the error limits indicated for this work are based on qualitative estimates of probable systematic errors and the effect of the scatter in the experimental data. Error limits for other work are not quoted since they are frequently statistical measures of precision and do not take into account the possibility of systematic errors.

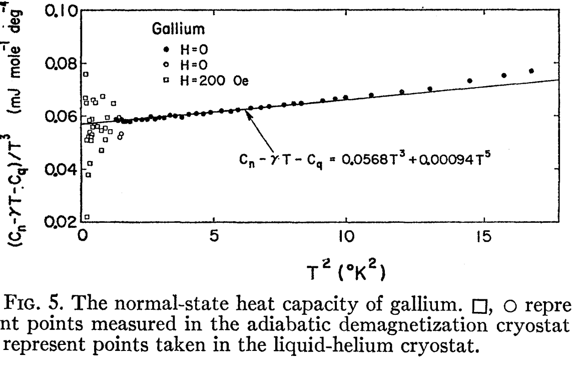

FIG. 5. The normal-state heat capacity of gallium. □, ○ represent points measured in the adiabatic demagnetization cryostat; ● represent points taken in the liquid-helium cryostat.

TABLE II. The normal-state heat capacity of gallium: $C_n = \alpha T^{-2} + \gamma T + A T^3 + B T^5$.

	α (mJ mole^{-1} deg)	γ (mJ mole^{-1} deg^{-2})	θ_0 (°K)	A (mJ mole^{-1} deg^{-4})	B (mJ mole^{-1} deg^{-6})
This work	$(4.3\pm0.3)\times10^{-4}$	0.596 ± 0.005	324.7 ± 2	0.0568 ± 0.001	$(9.4\pm1)\times10^{-4}$
Hammond and Knight[a]	4.35×10^{-4}				
Wolcott[b]		0.75			
Seidel and Keesom[c]		0.601	317	0.0608	9.2×10^{-4}

[a] See Ref. 8. [b] See Ref. 10. [c] See Ref. 9.

The observed nuclear quadrupole heat capacity agrees to within our estimated accuracy with that calculated from the nuclear quadrupole resonance measurements by Hammond and Knight.[8]

Seidel and Keesom[9] have measured C_n for gallium between 1.1 and 4.2°K. Their measured values are from 0.5 to 2% higher than those reported here, and they have represented their data over the entire range by Eq. (5), whereas these measurements deviate appreciably from Eq. (5) at 4°K. Their values of γ and B are in good agreement with this work, but there is a discrepancy of 7% in A. The large difference in the values of A is a consequence of the appreciable contribution to C_l made by the T^5 term at temperatures for which $C_l \lesssim \gamma T$.

The γ value reported by Wolcott[10] is in serious disagreement with the other determinations.

B. Superconducting State

It is apparent from Fig. 3 that the measured C_s does not include the nuclear quadrupole term observed in the normal state: at the lowest temperature of measurement C_s is only about one-fourth of C_q. The absence of this contribution to C_s has also been noted in indium[2] and mercury,[11] and is a consequence of the long spin-lattice relaxation time T_1 in the superconducting state. Hammond and Knight[8] have measured T_1 in normal gallium between 1.2 and 4.2°K and found $T_1T=0.5$ sec deg. For the lowest temperature at which C_n was measured this gives $T_1\approx3$ sec, comparable to the response time of the temperature-measuring circuitry, and consistent with the absence of any unusual time effects in the temperature drifts. Hebel and Slichter[12] and Hebel[13] have given a discussion of T_1 in the superconducting state based on the BCS theory[14] and involving an additional parameter r which is the ratio of the energy gap to the effective breadth of the energy levels. They predict a reduction in T_1 as a metal is cooled through the transition temperature, followed by an exponential increase in T_1 as the temperature is reduced further. The initial reduction in T_1 has been observed in gallium by Hammond and Knight.[8] Their measurements do not go to low enough temperatures to observe the predicted exponential increase in T_1 at $T\sim T_c/2$, but it has been observed in aluminum[15] and cadmium.[16] It is possible to set an approximate lower limit to T_1 from the heat-capacity experiments. As can be seen in Fig. 3, the highest temperature at which C_q would be a significant contribution to C_s is at $T^2\approx0.075$°K^2 or $T/T_c\approx0.25$. The periods of temperature drift between successive heat inputs were of approximately 30-sec duration, and the drift rate was close enough to constant to put a lower limit of about 60 sec to T_1. In the normal state at this temperature $T_1\sim1.5$ sec, and comparison of these two values with the curves given by Hebel[13] shows that $r\lesssim10$. A value of $r=10$ has been used to fit the experimental data on T_1 for both aluminum and cadmium. The value of r has been interpreted as a measure of the anisotropy of the energy gap and on this basis the anisotropy in gallium would be comparable to or greater than that in aluminum and cadmium.

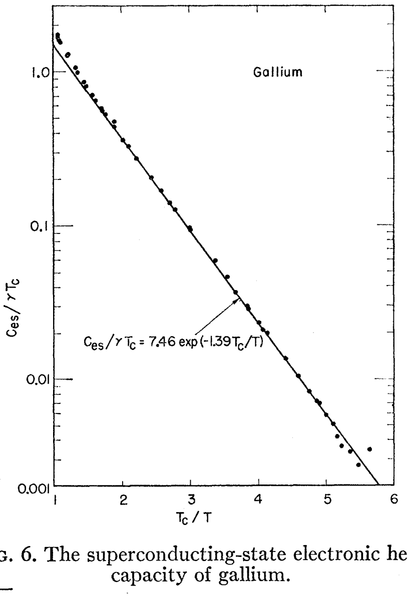

FIG. 6. The superconducting-state electronic heat capacity of gallium.

The electronic heat capacity C_{es} was obtained by using Eq. (5) and values of C_l from the normal-state

---

[8] R. H. Hammond and W. D. Knight, Phys. Rev. **120**, 762 (1960).

[9] G. Seidel and P. H. Keesom, Phys. Rev. **112**, 1083 (1958).

[10] N. M. Wolcott, Bull. Am. Phys. Soc. **1**, 289 (1956).

[11] N. E. Phillips, M. H. Lambert, and W. H. Gardner, International Conference on the Science of Superconductivity, Colgate University, August 1963 (to be published).

[12] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

[13] L. C. Hebel, Phys. Rev. **116**, 79 (1959).

[14] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[15] Y. Masuda and A. G. Redfield, Phys. Rev. **125**, 159 (1962).

[16] Y. Masuda, IBM J. Res. Develop. **6**, 24 (1962).

measurements. It is shown in Fig. 6 as a plot of $\ln(C_{es}/\gamma T_c)$ versus T_c/T. Between $T_c/T\approx 2$ and the lowest temperature points, at $T_c/T=5.5$, C_{es} has the form predicted by the BCS theory, $C_{es}/\gamma T_c=a\times\exp(-bT_c/T)$, but with $a=7.46$ and $b=1.39$ instead of the theoretical values for this temperature range, $a=8.5$ and $b=1.44$. The discrepancy between the theoretical and experimental values of a and b is typical of the behavior of other superconductors, but C_{es} follows an exponential temperature dependence to values of T_c/T at which aluminum and some other superconductors show positive deviations. These deviations have been attributed to anisotropy of the energy gap,[17] but the above argument based on T_1 suggests that the anisotropy in gallium is at least as great as that in aluminum.

The entropy and free-energy differences between the normal and superconducting states were found by extrapolating C_{es}/T to $T=0$ and carrying out the appropriate integrations. The entropies of the two states were equal to within 0.2% at the critical temperature. Critical fields calculated from the free-energy differences are shown in Fig. 7 as deviations from a parabolic critical field curve,

$$H_c/H_0=1-(T/T_c)^2, \tag{7}$$

where H_c is the critical field at the temperature T and H_0 is the critical field at the absolute zero. The free-energy difference at the absolute zero is $V_mH_0^2/8\pi$, where V_m is the molar volume, and was found to be 0.1627 mJ mole^{-1}.

TABLE III. The superconducting-state parameters of gallium.

	T_c (°K)	H_0 (Oe)	a	b	$\frac{C_{es}(T_c)}{\gamma T_c}$	$\frac{\gamma T_c^2}{V_mH_0^2}$
This work	1.078	58.9	7.46	1.39	2.44	0.169
Seidel and Keesom[a]	1.087	59.4	7.0	1.35	2.41	0.170
Goodman and Mendoza[b]	1.103	50.3				
Cochran and Mapother[c]	1.091					
BCS[d]			8.5	1.44	2.52	0.170

[a] See Ref. 9.
[b] B. B. Goodman and E. Mendoza, Phil. Mag. 42, 594 (1951).
[c] J. F. Cochran and D. E. Mapother, Phys. Rev. 121, 1688 (1961).
[d] See Ref. 14.

The superconducting-state parameters are summarized in Table III and compared with other experimental values and the predictions of the BCS theory. The two sets of calorimetric measurements are in good agreement in view of the difficulties associated with temperature measurements in this region. The discrepancy between the two sets of experimental values of a and b may be partly a result of the influence of the lower temperature points in this work.

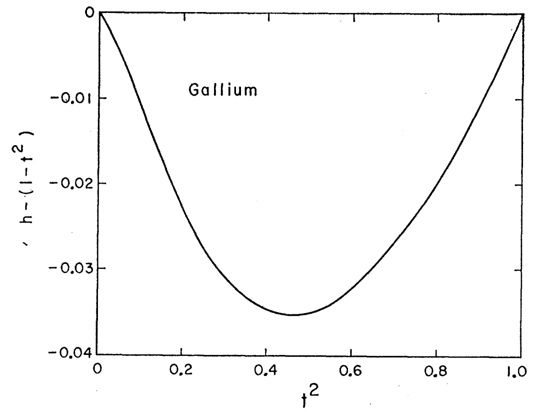

FIG. 7. The device of the reduced critical field of gallium from a parabola. $h=H_c/H_0$; $t=T/T_c$.

IV. THE HEAT CAPACITY OF CADMIUM

The sample was a 900-g single crystal grown under an inert atmosphere from 99.999% cadmium. The superconducting transition temperature, found by the method used in the gallium measurements, was $T_c=0.518$°K. This is in good agreement with the value reported recently by Martin[18] but is lower than most of the earlier values.

The heat-capacity points taken below 0.75°K in the adiabatic demagnetization apparatus are shown as a plot of C/T versus T^2 in Fig. 8. The normal-state data and the superconducting-state data are discussed separately in the following sections.

A. Normal State

The intercept of the straight line of Fig. 8 gives the value $\gamma=0.688$ mJ mole^{-1} deg^{-2}. Since C_l is only 24%

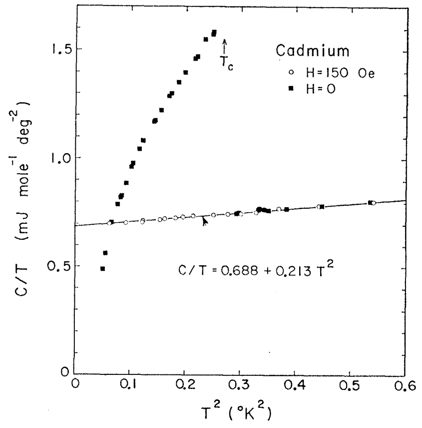

FIG. 8. The heat capacity of cadmium at $T<0.75$°K.

---

[17] For a summary of experimental and theoretical work related to this point, see J. Bardeen and J. R. Schrieffer in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 207.

[18] D. L. Martin, Proc. Phys. Soc. (London) 78, 1482 (1961).

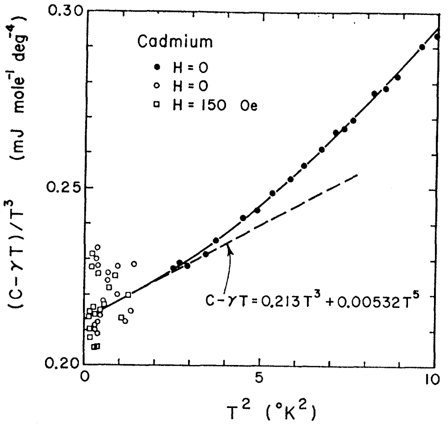

FIG. 9. The normal-state heat capacity of cadmium. □, ○ represent points measured in the adiabatic demagnetization cryostat; • represent points measured in the liquid-helium cryostat.

of C_n at 1°K, the slope does not give an accurate value of A and the slope of the straight line in the figure was obtained as described below. Figure 9 shows a plot of $(C-\gamma T)/T^3$ versus T^2. The points taken in the liquid helium cryostat have a much higher precision and are expected to have a higher accuracy than those taken in the adiabatic demagnetization cryostat, but they do not extend to low enough temperatures to define unambiguously the slope and intercept at $T^2=0$. We have taken the solid curve as the best fit to the data, and the dashed line, which has the same slope at $T^2=0$, determines the values of A and B. The value of θ_0 is 209.0°K and, as for gallium, the effects of dispersion become important at unusually low reduced temperatures. As shown in Fig. 10, θ is 4% less than θ_0 at $T=\theta_0/100$.

Table IV compares the normal-state parameters with other calorimetric data and with the values of A and θ_0 calculated from the elastic constants. The hexagonal metals have been noted for showing discrepancies between the values of θ_0 obtained by the two methods, and cadmium is typical in this respect. The earlier calorimetric measurements by Smith and Wolcott[19] and by Srinivasan[20] give $\theta_0=188$ and 189°K, in marked disagreement with the value $\theta_0=213$ from elastic constants.[21] The two other more recent calorimetric[18,22] measurements are in better agreement with the elastic constants although the agreement is not as good as has been found in a number of metals. The value obtained in this work is in satisfactory agreement with the elastic constants value.

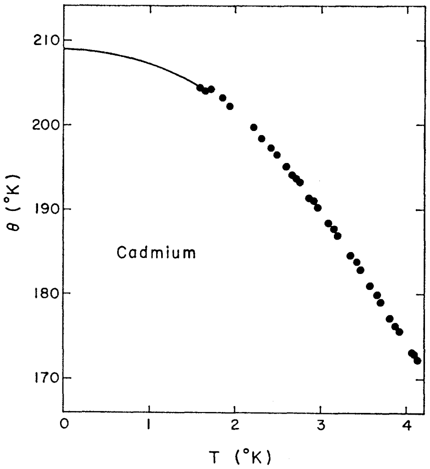

FIG. 10. The effective Debye temperature of cadmium. The curve is equivalent to the dashed line of Fig. 9.

The reason for the relatively large discrepancies between even the three most recent calorimetric values of θ_0 is made clear by the shape of the curve in Fig. 9. This shows that there are appreciable deviations from Eq. (3) at $T^2=1$°K^2 and from Eq. (4) at $T^2=5$°K^2.

TABLE IV. The normal-state heat capacity of cadmium, $C_n=T+AT^3+BT^5$.

	γ (mJ mole^{-1} deg^{-2})	θ_0 (°K)	A (mJ mole^{-1} deg^{-4})	B (mJ mole^{-1} deg^{-6})
Calorimetric measurements				
This work	0.688±0.006	209.0±2.3	0.213±0.007	0.00532±0.0005
Samoilov[a]	0.71			
Smith and Wolcott[b]	0.628	188	0.293	
Srinivasan[c]	0.636	189	0.288	
Martin[d]	0.685	204	0.229	
Rajdev and Whitmore[e]		219.5	0.184	0.0098
Elastic constants measurements				
Garland and Silverman[f]		213		

[a] B. N. Samoilov, Dokl. Akad. Nauk SSSR **86**, 281 (1952).
[b] See Ref. 19.
[c] See Ref. 20.
[d] See Ref. 18. The θ_0 value included in Table IV was actually interpreted by Martin as the effective Debye temperature in the interval covered by his experiments, 0.7 to 1.5°K.
[e] See Ref. 22.
[f] See Ref. 21.

---

[19] P. L. Smith and N. M. Wolcott, Phil. Mag. **1**, 854 (1956).

[20] T. M. Srinivasan, Proc. Indian Acad. Sci. Sect. A, **49**, 61 (1959).

[21] C. W. Garland and J. Silverman, Phys. Rev. **119**, 1218 (1960).

[22] D. Rajdev and D. H. Whitmore, Phys. Rev. **128**, 1030 (1962).

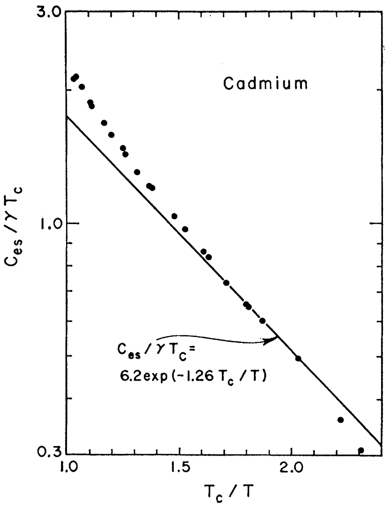

FIG. 11. The superconducting-state electronic heat capacity of cadmium.

Martin,[18] whose value of γ is in excellent agreement with this work, used Eq. (3) to analyze data extending up to $T^2=2.5$. This would tend to overestimate the limiting slope of a plot such as that of Fig. 8 and would consequently give too low a value for θ_0. Rajdev and Whitmore[22] used Martin's γ value and the method of Fig. 9 to analyze their liquid-helium temperature measurements. Their data are not precise enough to show clearly the curvature in the plot of $(C-\gamma T)/T^3$ versus T^2, and they assumed the validity of Eq. (4) up to $T^2=12$. This would be expected to lead to too low a value for the intercept and too high a value of θ_0. The discrepancies between the calorimetric values of θ_0 can therefore be attributed to the importance of dispersion effects in the lattice heat capacity at temperatures at which the electronic heat capacity is still a large part of the total.

TABLE V. The superconducting-state parameters of cadmium.

	T_c (°K)	H_0 (Oe)	a	b	$\frac{C_{es}(T_c)}{\gamma T_c}$	$\frac{\gamma T_c^2}{V_m H_0^2}$
This work	0.518	29.6	6.2	1.26	2.32	0.177
Goodman and Mendoza[a]	0.560	28.8				
BCS[b]			8.5	1.44	2.52	0.170

[a] See Ref. 25.
[b] See Ref. 14.

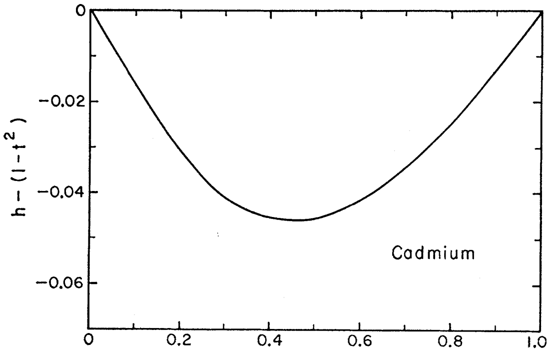

FIG. 12. The deviation of the reduced critical field of cadmium from a parabola. $h=H_c/h_0$; $t=T/T_c$.

The absence of a significant discrepancy between the calorimetric θ_0 reported here and that derived from the elastic constants is of importance in establishing the generality of the relation between the elastic constants and the T^3 term in the lattice heat capacity. Experimental tests of this relation are of interest in connection with suggestions that it is modified in metals by effects associated with the conduction electrons.[23,24] Furthermore, if agreement between the two values of θ_0 is generally found for those metals in which both can be measured, the elastic constants can be of use in the analysis of heat-capacity data for metals in which accurate calorimetric determinations of θ_0 are not possible. Obvious applications would be in searching for magnetic contributions to the heat capacity and for changes in lattice heat capacity at the superconducting transition.

B. Superconducting State

The experimental data do not extend to low enough temperatures to give an unambiguous evaluation of the superconducting state entropy. In extrapolating C_{es} to $T=0$ for this calculation it was assumed that C_{es} had the BCS form, $C_{es}/\gamma T_c=a\exp(-bT_c/T)$. An expression of this type has generally been found to give an adequate representation of experimental data in the region of importance for the entropy calculation. A plot of $\ln(C_{es}/T_c)$ versus T_c/T is given in Fig. 11. The lowest temperature points do not fall on a straight line. The line chosen to represent the limiting slope gives no weight to the two lowest points, but does give the same entropy for the normal and superconducting states at T_c. A line which gave approximately equal weight to all points at $T_c/T\geqslant 1.6$ led to an entropy discrepancy of 3% at T_c and it was therefore assumed that the two lowest points were in error.

The superconducting state parameters are given in Table V. Martin[18] has recently tabulated the experimental values of T_c and they are not repeated here. The only other experimental data which can be compared with this work are the critical field measurements of Goodman and Mendoza[25] and their H_0 value is included in the table.

Figure 12 shows the deviation of the critical field curve from a parabola. The deviation is negative and larger than has been observed in other superconductors. This is consistent with the established general trend in these deviations with decreasing T_c/θ_0.

---

[23] J. L. Warren and R. A. Ferrell, Bull. Am. Phys. Soc. **3**, 226 (1958).

[24] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **43**, 1005 (1962) [English transl.: Soviet Phys.—JETP **16**, 780 (1963)].

[25] B. B. Goodman and E. Mendoza, Phil. Mag. **42**, 594 (1951).