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Specific Heat of Lead in the Range from 2 to 8°K*

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The specific heat of pure lead has been measured in the normal and superconducting states between 2 and 8°K. The electronic contribution in the superconducting state, C_{es}, is derived using $\gamma = 3.00$ mJ/mole deg^2 taken from other sources. Near T_c, C_{es} is roughly proportional to $T^{3.5}$, but the dependence becomes more marked as the temperature is reduced. Our data do not conform to the T^4 dependence deduced from the critical-field curve by Decker, Mapother, and Shaw for $1.2 \leq T \leq 5$°K, although the critical field calculated from the difference $\Delta C = C_n - C_s$ agrees with the measured values to within 0.8%. The Debye temperature Θ is deduced from the normal-state results, and a plot of Θ versus T is given. The curve suggests that a maximum in Θ occurs near 1°K.

I. INTRODUCTION

LEAD is a so-called "strong-coupling" superconductor, and as such its properties are of particular interest for comparison with recent theories of superconductivity.[1,2] These theories are largely concerned with differences between the behavior of "weak-coupling" superconductors, which are fairly well understood in terms of the original BCS model,[3] and of metals like mercury, niobium, and lead, for which the older theory is inadequate. Although from a qualitative standpoint these two classes are readily distinguishable, quantitative distinctions between them are relatively subtle. With respect to the difference between the specific heats in the normal and superconducting states, $\Delta C = C_n - C_s$, it is therefore desirable to measure C_n and C_s with accuracy sufficient to specify ΔC to 1% or better. In strong-coupling cases this is very difficult, particularly near the superconducting transition, because of the overwhelming contribution of the lattice specific heat, which is common to both C_n and C_s. For example, in lead ΔC is at most a few percent of C_n for temperatures larger than 4°K. The maximum difference of 58.5 mJ/mole°K occurs at T_c, the transition temperature, where it is only 5.2% of C_n.

The best data[4] previously reported for lead in the range near T_c suffice to fix ΔC only within limits of ±10%. The present paper reports the results of measurements over the range from 2 to 8°K which are sufficiently precise to determine $C_n - C_s$ to within 1%. This work is complementary to the recent investigations of van der Hoeven and Keesom[5] and of Phillips, Lambert, and Gardner,[6] in which C_n and C_s were measured in the ranges 0.4–4.2°K and 0.3–0.8°K, respectively.

II. DESCRIPTION OF THE EXPERIMENT

Specific-heat measurements were made using the continuous-warming method, in which heat is added to a specimen at a constant rate and the resulting rate of increase of temperature is observed. A discussion of the experimental method, including a description of the thermometer-calibration procedure and an analysis of the errors encountered in the measurement, has been given by Cochran *et al.*[7] and need not be repeated here. Normal- and superconducting-state values of the specific heat were repeatable to 0.03% during any one low temperature run; the over-all accuracy of the data is estimated to be about 0.2%.[8] It should be noted that the critical temperature of lead, $T_c = 7.193$°K,[9] was used as a fixed point for thermometer calibration and was not measured in this experiment.

The specimen was 0.59 mole "superpure" polycrystalline lead.[10] The original ingot was swaged to a diameter of 0.48 in., cut to length, and then annealed for a week at 200°C. The residual resistance ratio of the resulting bar was in excess of 6×10^4.

During superconducting-state measurements the apparatus was surrounded by a "Mu-metal" shield[11] which reduced the magnetic field at the specimen to approximately 10^{-3} G. Normal-state data were obtained with the specimen immersed in a field of 10^3 G generated by a superconducting solenoid operating in its persistent-current mode.

III. RESULTS AND DISCUSSION

The 456 normal-state data points and 404 superconducting-state data points were fitted by the method

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[1] Y. Wada, Phys. Rev. **135**, A1481 (1964).

[2] J. Bardeen and M. Stephen, Phys. Rev. **136**, A1485 (1964).

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

[4] J. R. Clement and E. H. Quinnell, Phys. Rev. **85**, 502 (1952).

[5] B. J. C. van der Hoeven and P. H. Keesom, Phys. Rev. **137**, A103 (1965).

[6] N. E. Phillips, M. H. Lambert, and W. R. Gardner, Rev. Mod. Phys. **36**, 131 (1964).

[7] J. F. Cochran, C. A. Shiffman, and J. E. Neighbor, Rev. Sci. Instr. **37**, 499 (1966).

[8] This estimate includes systematic errors which are the same or nearly the same in both the normal and superconducting states. These errors, such as those associated with the choice of thermometer-calibration function, either cancel in taking the difference $C_n - C_s$, or, at worst, affect the difference in the same proportion as they do the specific heat itself.

[9] J. P. Franck and D. L. Martin, Can. J. Phys. **39**, 1320 (1961).

[10] According to the supplier (Semi-Alloys, Inc., Mt. Vernon, New York), the original ingot contained less than one part per million total impurities.

[11] Allegheny Ludlum Steel Corporation, Pittsburgh, Pennsylvania.

TABLE I. The coefficients b_n of the polynomial obtained from a least-squares fit of the specific-heat data in the form $C/T = \sum b_n T^{2n}$. The units are mJ/mole deg^2. Normal state: 1.848–8.000°K, 456 data points fitted with a rms fractional deviation of 6.1×10^{-4}. Superconducting state: 1.946–7.159°K, 404 data points fitted with a rms fractional deviation of 5.4×10^{-4}.

	Normal state: C_n/T	Superconducting state: C_s/T	Difference: $(C_n-C_s)/T$
b_0	1.8430463×10^{0}	-1.3136653×10^{0}	3.1567116×10^{0}
b_1	2.2182458×10^{0}	2.2369905×10^{0}	-1.8744680×10^{-2}
b_2	-8.3223769×10^{-2}	-6.9880072×10^{-2}	-1.3343697×10^{-2}
b_3	8.1100891×10^{-3}	8.1315359×10^{-3}	-2.1446830×10^{-5}
b_4	-2.8018966×10^{-4}	-3.2214374×10^{-4}	4.1954081×10^{-5}
b_5	5.0558488×10^{-6}	6.9721077×10^{-6}	-1.9162589×10^{-6}
b_6	-4.7756933×10^{-8}	-8.1862429×10^{-8}	3.4105496×10^{-8}
b_7	1.8550378×10^{-10}	4.0317529×10^{-10}	-2.1767145×10^{-10}

of least squares to polynomials in temperature. These polynomials represent the data within experimental error, the rms fractional deviation of the points from the smooth curve being about 6×10^{-4} in each case. The coefficients for C_n and C_s, and their differences which give a polynomial expression for C_n-C_s, are listed in Table I. Values of specific heat obtained by evaluating the polynomials at 0.25°K temperature intervals are listed in Table II.

In the overlapping temperature interval from 1.8 to 4.4°K, specific heats calculated from our normal-state polynomial agree with the normal-state values tabulated by van der Hoeven and Keesom[5] to 1%, the accuracy quoted for their measurement. On the other hand, specific heats calculated from the superconducting-state polynomial are systematically lower than the data listed by the above authors. The disagreement is about 6% for one sequence of values in their table, and about 2% for the other. Since our data do not extend below 1.85°K ($T_c/T \simeq 4$), they do not bear directly on the conclusions of van der Hoeven and Keesom for the temperature region $T_c/T > 5$.

TABLE II. Specific heats in mJ/mole deg calculated from the polynomials whose coefficients are given in Table I. The units of temperature are in °K.

T	C_n	C_s	$C_{es}/\gamma T_c$
2.00	19.67	13.92	0.0116
2.25	26.60	20.44	0.0273
2.50	35.14	28.73	0.0510
2.75	45.56	39.13	0.0844
3.00	58.24	52.03	0.129
3.25	73.64	67.92	0.187
3.50	92.29	87.36	0.258
3.75	114.7	110.9	0.344
4.00	141.7	139.3	0.444
4.25	173.9	173.1	0.558
4.50	211.7	213.0	0.688
4.75	255.9	259.6	0.834
5.00	307.0	313.5	1.00
5.25	365.4	375.3	1.19
5.50	431.4	445.3	1.41
5.75	505.4	524.0	1.67
6.00	587.4	611.6	1.96
6.25	677.7	708.1	2.28
6.50	776.4	813.3	2.62
6.75	883.2	927.0	2.97
7.00	998.0	1049.3	3.35
7.25	1112		
7.50	1249		
7.75	1384		
8.00	1527		

The contribution of the lattice to the normal-state specific heat can be calculated by subtracting the electronic contribution from the measured values. The calometric studies of van der Hoeven and Keesom[5] and of Phillips *et al.*[6] show that the electronic contribution to C_n is given by $C_{en} = \gamma T = 3.00T$ (mJ/mole °K).[12] The value for γ deduced from the critical-field measurements of Decker *et al.*[13,14] is 3.06 mJ/mole deg^2. The lattice specific heat defines a Debye temperature Θ in the conventional way via the Debye function (tabulated by Giguere and Boisvert[15]). Figure 1 displays Θ as a function of T derived from our data on the basis of the above calorimetric value for γ. Also shown are limiting values for Θ at $T=0$°K obtained from specific-heat measurements[5,6] and from data on the velocity of sound.[16] A striking feature of the curve in Fig. 1, which cannot be attributed to experimental uncertainties,[17] is the decided upturn near 2°K. This suggests the possibility of a maximum in the Debye temperature near absolute zero, similar to that observed by Martin[18] for gold.

The electronic contribution to the specific heat in the superconducting state can be obtained as usual by assuming that the lattice term is the same as in the normal state. Thus,

$$C_{es} = C_s - (C_n - \gamma T) = \gamma T - \Delta C.$$

Figure 2 shows the result of this calculation, based on our data and on the value 3.00 mJ/mole deg^2 for γ. As one can see from Table II, ΔC and γT are nearly equal at low temperatures; for instance, at 2°K they differ by only 2%. The value deduced for C_{es} is therefore very sensitive to the exact values chosen for each of these quantities. Since ΔC is a large fraction of the total specific heat in the low-temperature region and can be

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[12] Professor Phillips has informed us that a revised analysis of the data in Ref. 6 yields the value $\gamma = 3.02$ mJ/mole deg^2.

[13] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).

[14] Decker *et al.* obtain γ from the coefficients in their power series for $H_c(T)$. A more satisfactory procedure is to fit the low-temperature points to the limiting theoretical expression $H_c^2 = H_0^2 - 4\pi\gamma T^2/V_m$, where V_m is the molar volume. We have re-examined their data in this way and find $\gamma = 2.99$ mJ/mole deg^2, which is in even better agreement with the calorimetric values. The improvement may be fortuitous, however, since only seven of their data points are at a sufficiently low temperature that no curvature can be seen in an H_c^2-versus-T^2 plot.

[15] P. Giguere and M. Boisvert, *Tables des Fonctions Thermodynamiques de Debye* (Les Presses de l'Universite Laval, Quebec, 1962).

[16] D. L. Waldorf and G. A. Alers, J. Appl. Phys. 33, 3266 (1962).

[17] The small uncertainty in $\Theta(T)$ is almost entirely due to uncertainty in the value of γ. The choice $\gamma = 3.06$ mJ/mole deg^2 would elevate our lowest temperature value (at $T=1.85$°K) to 105.3°K, an increase of only 0.4%.

[18] D. L. Martin, Phys. Rev. **141**, 576 (1966).

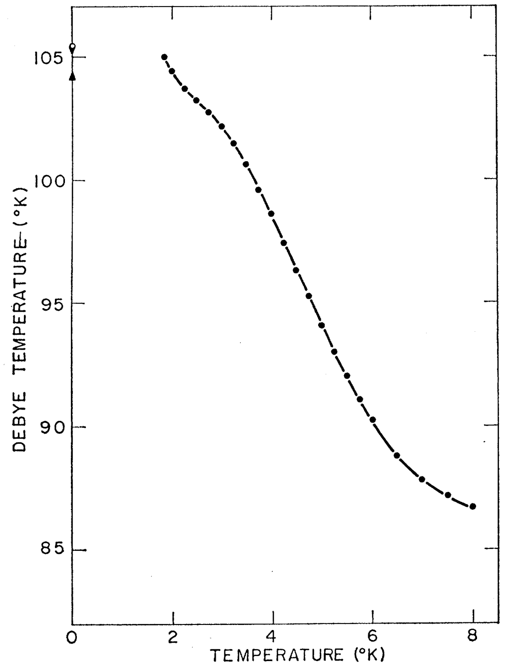

FIG. 1. Debye temperature Θ as a function of T. ● this work; ○ Ref. 5; ▲ Refs. 6, 12; ▼ Ref. 16.

determined relatively accurately, the accuracy of the curve for C_{es} depends almost entirely on the validity of the choice for γ. For example, using the value $\gamma = 3.06$ mJ/mole deg^2 of Decker *et al.* would raise the curve by about 50% at 2°K. Figure 2 includes two points, indicated by crosses, which were calculated on this basis. As the temperature rises, C_{es} increases very rapidly, and the sources of error become more evenly divided between γ and ΔC. Near T_c we estimate that C_{es} can be specified with an uncertainty of less than 2%.

As Fig. 2 clearly shows, C_{es} does not follow the prediction of the original BCS theory. This is in qualitative agreement with both theoretical expectation and earlier experimental results.[5,13] Near T_c, the observed ratio $C_{es}/\gamma T_c$ is larger than the BCS value, a feature which lead shares with most superconductors and which is therefore not characteristic of the "strong-coupling" family. (It has been noted earlier[19] that the extent of this excess can be correlated in a simple way with the ratio of T_c to the Debye temperature.) The excess is usually characterized by the ratio of the jump in specific heat at the transition temperature to γT_c. As is shown in Table III, our value for the ratio is in excellent agreement with that calculated from the magnetic data,[13] and with the calorimetric value obtained in earlier work.[19] (The agreement between the calorimetric and magnetic determinations promotes confidence in the calibration procedures used to obtain temperatures in the awkward range 4.2–7.2°K.) Near T_c, C_{es} varies approximately as $T^{3.5}$, but as the temperature is lowered the dependence becomes stronger. At the lowest temperatures reached in this experiment, C_{es} varies roughly as $T.^8$ These simple power laws should not be taken as anything but a rough guide to the temperature dependence, since the curvature on a log-log plot is very marked over the entire range 2–7.2°K. This is a point of substantial disagreement with the results deduced by Decker *et al.* by differentiating the critical-field curve twice. They find a very good fit to the function $C_{es} = 1.635T^4$ in the range 1.2–5°K. At 2°K, the value of C_{es} they deduce is almost three times as large as ours, if 3.00 mJ/mole deg^2 is chosen for γ, and about 50% larger if 3.06 is used. (See Ref. 14, however.) This disagreement is compatible with the estimates made by Decker *et al.* for the error involved in the differentiation of their smoothed data. Van der Hoeven and Keesom have also deduced C_{es} from calorimetric measurements and report that $C_{es} \propto T^3$ for $T \leq 1.5$°K. Unfortunately, our measurements do not extend quite this low in temperature, but stop at 1.8°K, and no direct comparison can be made.

TABLE III. Jump in the specific heat of lead at the critical temperature, in mJ/mole °K.

Source	$\Delta C = C_s - C_n$	$C_{es}/\gamma T_c$
Shiffman *et al.* (Ref. 19)	57.7±0.6	3.67
Decker *et al.* (Ref. 13)	58.1±0.7	3.69
This work	58.5±0.9	3.71
BCS theory		2.43

To establish the degree of thermodynamic consistency between calorimetric and magnetic data, it is better, in some respects, to integrate the specific heat than to differentiate the critical field. In particular, where

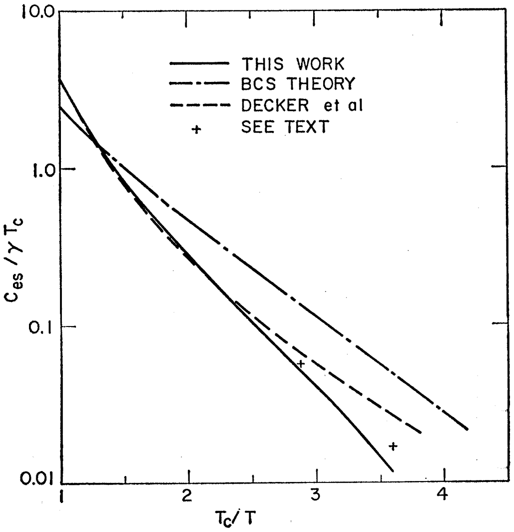

FIG. 2. The electronic specific heat in the superconducting state as a function of inverse reduced temperature T_c/T.

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[19] C. A. Shiffman, J. F. Cochran, and M. Garber, J. Phys. Chem. Solids 24, 1369 (1963).

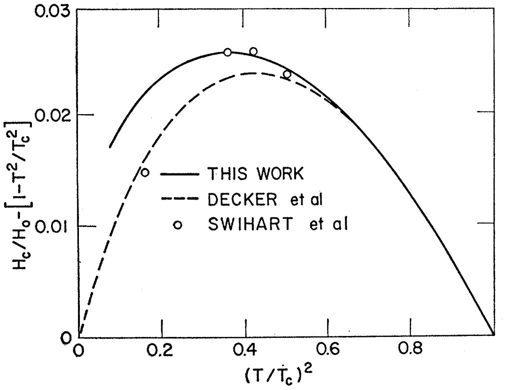

FIG. 3. Comparison between the measured critical field and the values deduced by integrating the specific-heat data. The ordinate is the difference between the reduced field H_c/H_0 and a reference parabola $1-T^2/T_c^2$; the abscissa is the square of the reduced temperature. Both experimental curves are based on $H_0=802.6$ G, determined by Decker *et al.* (Ref. 13). Points representing the theoretical calculation of Swihart *et al.* (Ref. 21) are based on $H_0=790$ G.

smooth curves have been fitted to the data, the result is less sensitive to the choice of fitting function. We have therefore calculated a critical-field curve from our data, using the thermodynamic relation

$$H_c^2(T)=(-8\pi/V_m)\int_{Tc}^{T}dT\int_{Tc}^{T}dT(C_n-C_s)/T.$$

The result is given in Fig. 3 in terms of the deviation of the reduced critical field, $h=H_c(T)/H_0$, from a parabolic law, $h=1-(T/T_c)^2$. The dashed curve is taken from Decker *et al.*,[13] who find $H_0=802.6$ G.[20] The solid curve is derived from our data, using the same value for H_0. At the lowest temperatures, the discrepancy between the derived and measured values of H_c is 0.8%, which is compatible with uncertainties in the specific-heat measurement and in the subsequent integrations. For the sake of completeness, the figure also includes the values calculated by Swihart, Scalapino, and Wada,[21] using the strong-coupling theory of Wada.[1] These points are normalized by a different value for H_0, 790 G, which Swihart *et al.* determine from the solution of the gap equation at absolute zero and from the observed value of the energy gap at $T=0$. The agreement with the experimental curves is very striking. As experience with the differentiation of the empirical critical-field curve indicates, a theoretical calculation of C_{es} itself may be required before the most meaningful comparison with the specific-heat data can be made.

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[20] As Decker *et al.* (Ref. 13) emphasize, this value is based on the largely intuitive rule that the thermodynamic critical field lies midway between the increasing- and decreasing-field branches of the hysteresis loops observed in the magnetization curves at low temperatures. If one takes the view that the sharp rise in magnetization in increasing fields determines the true transition field, one finds $H_0=805.7$ G.

[21] J. C. Swihart, D. J. Scalapino, and Y. Wada, Phys. Rev. Letters **14**, 106 (1965).