Specific Heat of Lead and Lead Alloys Between 0.4 and 4.2°K*

B. J. C. van der Hoeven, Jr. and P. H. Keesom

Purdue University, Lafayette, Indiana

(Received 10 August 1964)

The specific heat of a pure single crystal and a pure polycrystalline sample of lead has been measured between 0.4 and 4.2°K. For the coefficient of the normal-state electronic term γ, a value of (3.00 ± 0.04) mJ/mole deg^2 is found. The value for the Debye parameter at 0°K, Θ_0, is (105.4 ± 0.8)°K. Below 1.5°K, the superconducting-state specific heat C_s could be represented by a T^3 law, with a slope 5% larger than that of the normal-state specific heat C_n. As a result, below 1.5°K the superconducting-state electronic specific heat C_{es} followed a T^3 law, in disagreement with the exponential behavior predicted by the Bardeen-Cooper-Schrieffer theory. In an effort to investigate the anomalously large values of C_{es}, two samples of lead alloyed with 1.76% indium and 5.93% indium were measured. For the 1.76% In sample the anomaly persists, but it disappears for the 5.93% In sample. Tentatively it can be concluded that energy-gap anisotropy is able to explain the lead results.

INTRODUCTION

IN a letter to the editor[1] the results were reported of measurements of the specific heat of lead between 0.4 and 4.2°K. It was observed that at the lowest temperatures the specific heat of the electrons in the superconducting state, C_{es}, was anomalously large and could be described with a T^3 law. Several different theories could be considered in explaining this behavior. Energy-gap anisotropy indicates one possibility. Another suggestion has been made by Werthamer[2] on the basis of an electron-phonon interaction term in the normal-state specific heat.

If the anomalous specific heat of lead can be explained on the basis of energy-gap anisotropy, this anisotropy should be removed by alloying, as has been suggested by Anderson.[3] For this reason, the specific heat of lead with 1.76% indium and with 5.93% indium was measured. Indium was chosen for two reasons. First of all, it is soluble in lead over a wide range. In addition, if the reduced values of the energy gap should occur on the small bits of Fermi surface of lead extending beyond the second Brillouin zone, then alloying with lower valent indium may be able to displace those portions of the Fermi surface to lower zones. Reported here are more recent measurements of the low-temperature specific heat of very pure lead, and two lead-indium alloys. Also, residual resistivity measurements were made for each of the samples, and estimates of the electron mean free path are given.

EXPERIMENT

The apparatus used was the He^3 cryostat described previously.[4] A germanium thermometer, similar in composition to one discussed in an earlier publication,[5] was used for the pure single crystal Pb, the polycrystal-

line Pb and the Pb+5.93% In measurements. For Pb+1.76% In, a nominal 10 Ω, $\frac{1}{10}$-W Allen-Bradley carbon resistor was used and with this thermometer the pure polycrystalline lead was rechecked. The calibration of the thermometers between 0.4 and 1.2°K was based on the 1962-He^3 temperature scale of Sydoriak and Roberts.[6] Between 1.0 and 4.2°K the 1958-He^4 temperature scale[7] was used. An expansion of $1/T$ in powers of $\log R$ up to $(\log R)^3$ was done using the method of least squares described by Moody and Rhodes.[8]

The measurements of pure lead were done in zero magnetic field and in a field of 1300 G for the single crystal and 3000 G for the polycrystalline sample. For the two alloys, measurements were done in zero field and 17 000 G, using a set of high magnetic field cans described in an earlier publication.[9] Immediately after each specific-heat run the thermometers were calibrated in zero field and in 1300, 3000, or 17 000 G, according to the field used in the measurement. All measurements were carried out in a sequence of increasing field so that any possibility of trapped flux was avoided.

The systematic error in the specific heat due to inaccuracies in the temperature scale, as well as addenda corrections, heater resistance, current, and timing errors should not exceed $\pm2\%$ at the lowest temperature, and $\pm1\%$ at 4°K. Error limits stated for experimental quantities are those found from random scatter of the data, which is observed to be $\pm1\%$ over the entire temperature range.

SAMPLES

The pure polycrystalline lead sample (0.877 moles) of 99.9999% purity and the pure single crystal lead sample (0.828 moles) of 99.999% purity were very

* Work supported by U. S. Army Research Office-Durham.
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[6] S. G. Sydoriak, T. R. Roberts, and R. H. Sherman, in *Proceedings of the Eighth International Conference on Low-Temperature Physics*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963).
[7] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **64A**, 1 (1960).
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kindly furnished by Dr. G. A. Alers. The measurements referred to in the letter were made with a less pure polycrystalline sample and had much greater scatter in the specific-heat data. The results quoted here are those of the very pure polycrystalline and the single crystal Pb samples combined. The Pb+1.76% In sample (0.294 moles) and the Pb+5.93% In sample (0.325 moles) were prepared by addition of the appropriate amount of semiconductor grade indium shot to pure molten lead in a graphite boat. The samples were then vigorously stirred, solidified, and then annealed *in vacuo* for several weeks at 290°C. Total correction for the heat capacity of the addenda was less than 0.7% of the total heat capacity of each of the four samples in the superconducting state at the lowest temperature.

RESULTS

The specific heat of a superconductor in the normal state C_n is given by

$$C_n = C_{en} + C_{ln} + C_{int}, \qquad (1)$$

where $C_{en}(=\gamma T)$ is the normal state electronic term, C_{ln}

TABLE I. Specific heat of pure single crystal lead and pure polycrystalline lead between 0.4 and 4.2°K (C in mJ/mole deg).

T (°K)	C_s	T (°K)	C_n
0.363	0.090	0.431	1.44
0.379	0.098	0.485	1.67
0.395	0.116	0.545	1.90
0.434	0.147	0.616	2.24
0.498	0.221	0.741	2.90
0.588	0.362	0.908	3.96
0.667	0.527	1.680	13.0
0.768	0.814	1.907	17.6
0.900	1.303	2.238	26.1
1.067	2.19	2.440	32.8
1.175	2.93	2.658	41.2
0.472	0.192	2.889	51.9
0.526	0.261	3.129	65.4
0.609	0.401	3.376	82.3
0.700	0.602	3.700	109
0.827	0.998	4.072	149
0.964	1.57	4.41	195
1.098	2.35	1.004	4.71
1.272	3.68	1.168	6.23
1.408	5.00	1.282	7.46
1.578	7.07	1.414	9.09
1.753	9.72	1.546	11.0
1.958	13.8	1.716	13.8
2.180	19.5	1.819	15.8
2.366	25.3	1.983	19.4
2.514	30.9	2.046	21.0
2.662	37.2		
2.851	46.9		
3.004	55.9		
1.357	4.44		
1.723	9.20		
2.032	15.3		
2.529	30.6		
2.818	43.1		
3.158	65.6		
3.347	76.2		
3.599	97.9		
3.889	128		
4.117	157		
4.45	209		

is the lattice specific heat in the normal state, and C_{int} represents any contribution due to electron-lattice interactions. Normally the effect of the lattice on the electrons is included in γ, by means of the effective mass m^*. Hence, one usually assumes that C_{int} is negligibly small. Calculations by Eliashberg[10] and more recently by Werthamer[2] have indicated, however, that electron interactions with longitudinal and transverse phonons may introduce a term proportional to $T^3\ln(\Theta/T)$ in the normal-state specific heat. For the present analysis this term will be neglected, but consideration will be given to it at a later point in this article.

From the Debye theory of lattice specific heats, one obtains for C_{ln} at low temperatures

$$C_{ln} = \alpha T^3 + \beta T^5 = 1944[T/\theta(T)]^3 \text{ J/mole deg}.$$

Hence, C_n may be rewritten

$$C_n = \gamma T + \alpha T^3 + \beta T^5.$$

In the superconducting state, the specific heat, C_s, is written

$$C_s = C_{es} + C_{ls},$$

where C_{es} is that contribution due to the superconducting electrons, and C_{ls}, the superconducting state lattice specific heat. The Bardeen-Cooper-Schrieffer (BCS) theory calculated that C_{es} should have the form

$$C_{es} = a\gamma T_c \exp(-bT_c/T).$$

Moreover, it predicts that the lattice specific heat in the superconducting state, C_{ls}, should be equal to that in the normal state C_{ln}. Thus, one can write for sufficiently low temperatures

$$C_s = a\gamma T_c \exp(-bT_c/T) + \alpha T^3 + \beta T^5.$$

The results for the specific heat of both pure lead samples below 2°K are plotted in Fig. 1 and representative values are listed in Table I over the entire temperature range of measurement. Below 3°K, the average specific heat of both samples in the normal state is
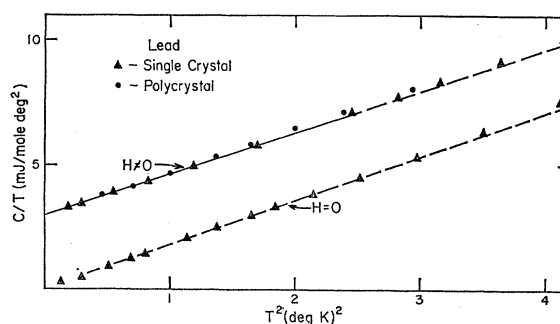

FIG. 1. Specific heat of pure lead below 2°K plotted as C/T versus T^2.

[10] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **43**, 1005 (1964) [English transl.: Soviet Phys.—JETP **16**, 780 (1963)].

given by

$$C_n = (3.00 \pm 0.04)T + (1.66 \pm 0.04)T^3$$
$$+ (0.16 \pm 0.008)T^5 \text{ mJ/mole deg.} \quad (2)$$

Several different sets of measurements were done on both samples over the temperature range from 0.4–4°K. From set to set, the measurements showed deviations up to 2% in the normal-state specific heat below 2°K. These differences are probably due to difficulties in calibrating the resistance thermometers. Both thermometers used, a germanium and a carbon composition thermometer, are magnetic field-dependent, and were recalibrated for each magnetic field. However, it was not possible to use the paramagnetic salt thermometer in these cases. Apparently the absence of this additional check during the calibration introduces uncertainties which are reflected in the specific-heat data.

It is expected that formula (2) represents the specific heat of lead within 1%. Magnetic field data[11] yield a value of γ, the coefficient of the linear term in (2) equal
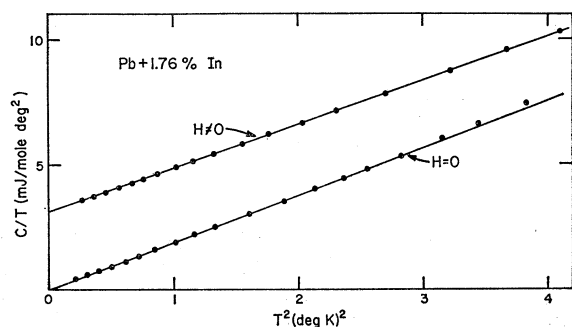

FIG. 2. Specific heat of Pb+1.76% In below 2°K plotted as C/T versus T^2.

to (3.06+0.04). The coefficient of the cubic term in T corresponds to a Debye parameter at 0°K, θ_0, of (105.4±0.8)°K. This is in agreement with the results derived from the velocity of sound measurements[12] for θ_0 of 105.3°K.

In Figs. 2 and 3 are plotted the specific heat of both alloys below 2°K. In the normal state below 3°K, the specific heat of the Pb+1.76% In alloy could be represented by

$$C_n = (3.05 \pm 0.03)T + (1.79 \pm 0.04)T^3$$
$$+ (0.008 \pm 0.005)T^5 \text{ mJ/mole deg.}$$

Similarly for the Pb+5.93% In alloy,

$$C_n = (2.97 \pm 0.03)T + (1.86 \pm 0.04)T^3$$
$$+ (0.007 \pm 0.005)T^5 \text{ mJ/mole deg.}$$

The coefficients of the T^3 terms above yield a value of Θ_0 for the 1.76% sample of (102.8±0.8)°K, and for the 5.93% sample of (101.5±0.8)°K.

[11] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).
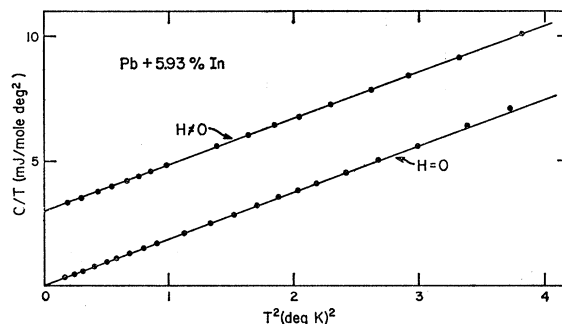[12] D. L. Waldorf and G. A. Alers, J. Appl. Phys. **33**, 3266 (1962).

FIG. 3. Specific heat of Pb+5.93% In below 2°K plotted as C/T versus T^2.

Below 1.5°K, the specific heat in the superconducting state C_s for both pure lead samples can be represented by a T^3 law, with a coefficient of 1.76 mJ/mole deg[4]. Similarly, the two alloys can be represented by a T^3 law in the same temperature range with a coefficient of 1.84 mJ/mole deg[4] for Pb+1.76% In, and 1.86 mJ/mole deg[4] for Pb+5.93% In. Above 1.5°K, both a T^5 lattice term and the exponential electronic term begin to contribute to C_s, causing a deviation above the T^3 law.

For all four samples the electronic specific heat in the superconducting state C_{es} was calculated in the following manner:

$$C_{es} = C_s - C_n + \gamma T.$$

In Fig. 4 is plotted $\ln(C_{es}/\gamma T_c)$ versus T_c/T for the two alloys and the average of the pure samples. T_c has been calculated for each sample according to the following expression,

$$T_c = 1.14\Theta_0 \exp[-1/(N(0)V)],$$

where $N(0) \propto \gamma$ and the interaction potential V is
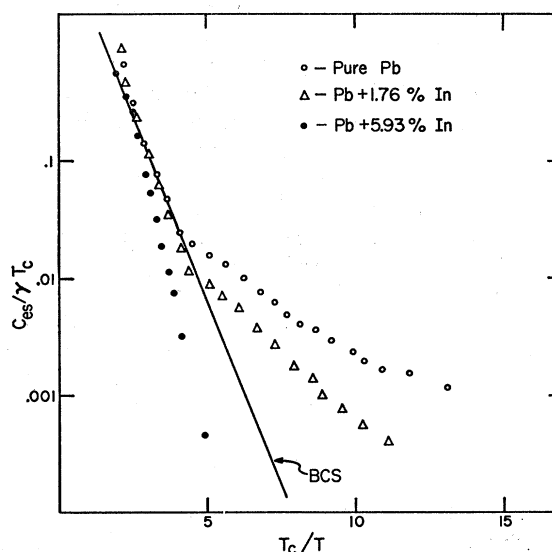

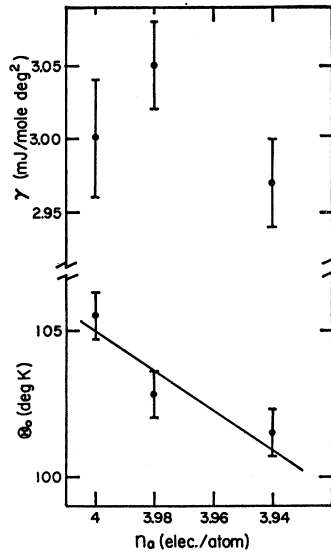FIG. 4. C_{es} plot for pure lead and the two alloys.

FIG. 5. γ and Θ_0 as a function of electron/atom ratio n_a.

assumed constant. The assumption regarding V is probably incorrect. Gayley et al.,[13] have shown that corrections to V will be such as to decrease the change in T_c in comparison with those calculated from the above expression. However, the shift in the C_{es} curve due to changes in T_c is not very large, and, as a result, recalculation of T_c on the basis of a change in V introduces only a second-order shift in the curve, which is negligible compared with the experimental scatter.

It is interesting to note that critical field measurements by Decker et al.[11] which are now supported by Shiffman et al.,[14] indicate a value of the specific-heat jump for pure lead at T_c larger than the BCS prediction. This implies a trend of C_{es} above the BCS value near T_c, which also follows from the present results for C_{es} below $T_c/T=3$.

A plot of Θ_0 and γ versus electron/atom ration n_a is given in Fig. 5, assuming lead to be 4 and indium 3 valent. The dependence of γ is consistent within experimental error with the simple relation, $\gamma \propto n_a^{1/3}$. The relation between Θ_0 and n_a is in agreement with observations by Gayley et al., for tin alloys, and with Rayne[15] for copper alloys, although there does not appear to be a satisfactory theory for this effect.

The resistivity was measured of thin ribbons (0.14 mm thick) made from each of the samples, except the single crystal. The ratio of room temperature resistivity over the resistivity at 8°K, $\rho_{RT}/\rho_{8°K}$, was greater than 4000 for the pure polycrystalline sample, 17.4 for Pb+1.76% In, and 6.4 for Pb+5.93% In. Using the relations between the mean free path, λ, and the resistivity ρ,

$$1/\rho = Ne^2\lambda/(m^*\bar{v}_0),$$

and setting the drift velocity $\bar{v}_0$ equal to the Fermi velocity of the metal, the following values of the mean free path were found: Pure Pb, $\lambda > 10^{-3}$ cm; Pb+1.76% In, $\lambda = 3.3 \times 10^{-6}$ cm; Pb+5.93% In, $\lambda = 1.1 \times 10^{-6}$ cm. The effective mass of the electrons, m^*, was determined from γ, yielding a value of $m^*/m = 2.00$.

The electron mean free path of the electrons has been calculated for purposes of comparing the coherence length of the superconducting electrons of the pure material ξ_0 with λ of the alloys. From Pippard[16] comes the relation,

$$\xi_0 = hv_0/[\pi\epsilon(0)],$$

where $2\epsilon(0)$ for lead is equal to $4.1kT_c$, $\bar{v}_0$ is the drift velocity determined above, and T_c for lead is 7.19°K. In this manner, ξ_0 is found to be 1.5×10^{-5} cm.

DISCUSSION

For the purpose of thermodynamic consistency, it is interesting to compare the specific-heat results with the results of magnetic measurements. Normally one integrates the specific heat differences, $\Delta C/T = (C_n - C_s)/T$, from 0°K to T_c, in order to obtain the entropy difference, $\Delta S(T)$. $\Delta S(T)$ is then integrated to yield the critical field, $H_c(T)$;

$$H_c^2(T) = \frac{8\pi}{V_m} \int_{T_c}^{T} S(T)dT,$$

where $V_m = 17.86$ cm³/mole for lead. However, as these measurements of the specific heat of lead extend only up to 4°K, it is impossible to obtain a value of H_0, the value of $H_c(T)$ at 0°K. On the other hand, by use of the following relation:

$$H_c^2(T) = H_0^2 - \frac{8\pi}{V_m} \int_0^{T} dT \int_0^{T} (\Delta C/T)dT,$$

setting H_0 equal to 802.6 G, the value found by Decker et al.,[11] it is possible to compare the magnetic data with the specific heat results. Interesting in this manner, the agreement between calculated and measured values of $H_c(T)$ is within 0.1 G up to 2°K, and increases slowly above this temperature. It should be emphasized that one expects such a calculation to be very accurate below 1.5°K, since the magnitude of ΔC below this temperature is the same as C_n and thus has the same relative error. However, at higher temperatures, ΔC becomes increasingly inaccurate, approaching only a few percent of either C_n or C_s at the highest temperatures. Thus, it is not surprising that the agreement between calorimetric and magnetic data is excellent below 2°K. In fact, below 1°K, the calorimetric results should be more accurate than magnetic data for interpreting quantities such as C_{es}.

A possible explanation for the low-temperature results might be found in an anisotropic energy gap. This has

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[16] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950).

already been observed for other metals, e.g., aluminum, but not of such a large magnitude. The BCS expression for $C_{es}/\gamma T_c$, equal to $a \exp(-bT_c/T)$, predicts that the values of a and b should be 8.5 and 1.44, respectively. The quantity a is related to the density of states of superconducting electrons near the Fermi surface, and b to the energy gap, $2\epsilon(0)$. Following Goodman,[17] the specific-heat energy gap at 0°K may be estimated by

$$2e(0) = (b/1.44)(3.50kT_c).$$

In this manner the C_{es} curve may be split up into two slopes representing two energy gaps; one with $a = 10.7$ and $2\epsilon(0) = 4.1kT_c$, and a smaller gap with $a = 0.1$ and $2\epsilon(0) = 1.1kT_c$. The larger gap value, $4.1kT_c$, is consistent with that found from tunneling[18] and infrared absorption[19] measurements, and has recently been theoretically predicted by Wada[20] from considerations of strong coupling superconductors.

Anderson[3] suggested that if anisotropy is the source of these anomalies, then dilute alloying of these materials should remove the anisotropy when the mean free path λ becomes of the order of the coherence length of the pure material ξ_0. It is apparent that for the case of Pb+1.76% In, where λ is about 20% of ξ_0, the anomaly persists. It does, however, disappear for the case of Pb+5.93% In, where λ is approximately 7% of ξ_0. Moreover, Goodman[21] remarked that measurements of the specific heat of aluminum alloys indicate that the anisotropy, although decreased, still persists even if λ is reduced to 5% of ξ_0. The conclusion is that anisotropy may very well explain the anomalous specific heat of lead. However, it then appears as if Anderson's criterion for the removal of anisotropy in dirty superconductors, namely, when $\lambda \sim \xi_0$, must be modified such that λ becomes a few percent of ξ_0.

The foregoing discussion has been made with the implicit assumption that the anomalous specific heat of lead originated in a temperature dependence of C_{es} different from the experimental BCS behavior. An entirely different approach to this problem has been proposed by Werthamer,[2] who attributes the anomaly to the normal-state specific heat. He expanded the

normal-state electron interaction with longitudinal phonons, originally calculated by Eliashberg,[10] to include the interaction with transverse phonons as well. Depending on the magnitude of these two interactions, which both yield contributions to the specific heat of the form $T^3 \ln(\Theta/T)$, but of opposite sign, a positive or negative term will be introduced in the expression for C_n. This is the C_{int} term included in Eq. (1). Such a contribution has the added advantage of being able to describe not only the pure lead results, but also the anomaly in the specific heat of indium.

There appear however to be two problems associated with this theory. For both the case of indium and lead, the Θ_0 value determined from the normal state specific heat, neglecting any interaction terms, is in excellent agreement with the value of Θ_0 determined from velocity of sound measurements. This would seem to imply that the T^3 term in the normal state is entirely due to the lattice, and that any additional terms, T^3 in nature, are negligible.

Moreover it is not clear from Werthamer's calculations if one expects the C_{int} term to disappear upon alloying. The lead anomaly disappears with alloying. On the other hand, several measurements have been made in this laboratory of the specific heat of indium alloyed with up to 1% tin and up to 2% bismuth. Using the results of Chanin et al.,[22] for an estimate of the reduction in λ due to bismuth added into indium, a value of λ for the In+2% Bi sample is found. This value is 6% of ξ_0 for pure indium. Nonetheless, the indium specific heat anomaly still persists. It seems therefore that this theory is unable to explain both indium and lead.

Tentatively, it can be concluded that energy gap anisotropy is able to explain the lead results, but that the anomalous specific heat of indium has yet to be resolved.

Note added in proof. Dr. Werthamer informed us of an error in sign in his article at "a crucial point, and that the corrected result implies transverse and longitudinal phonons contributing to a possible specific heat anomaly with the *same* sign."

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[18] I. Giaever, H. R. Hart, Jr., and K. Megerle, Phys. Rev. 126, 941 (1962).
[19] D. M. Ginsberg, P. L. Richards, and M. Tinkham, Phys. Rev. Letters 3, 337 (1959).
[20] Y. Wada, Rev. Mod. Phys. 36, 253 (1964).
[21] B. B. Goodman, Rev. Mod. Phys. 36, 198 (1964).
[22] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. 114, 719 (1959).