Low-Temperature Specific Heat of Indium and Tin*

C. A. BRYANT† AND P. H. KEESOM‡
Department of Physics, Purdue University, Lafayette, Indiana
(Received March 9, 1961)

The heat capacities of indium and tin were measured between 0.4 and 4.2°K. In the normal state, the specific heat could be represented by $AT^{-2}+\gamma T+\alpha T^3+\beta T^5+\mu T^7$. For Sn, in molar millijoule units, $A=0$; γ, the coefficient in the electronic term, is 1.80; $\alpha=0.242$, corresponding to a Debye temperature, θ_0, of 200°K; $\beta=0.004$; and $\mu=0.00014$. For In, A, the coefficient of a nuclear electric quadrupole term, is calculated to be 8.97×10^{-4} from resonance data; $\gamma=1.61$ for one ingot and 1.59 for another; $\theta_0=109°$ and 108°K; and $\beta=0.008$. In the superconducting state, the specific heat of Sn could be expressed as the normal lattice term plus an electronic term of the form $a\gamma T_c\exp(-bT_c/T)$, with $T_c=3.70$°K (0.02 deg lower than found in a magnetic measurement), $a=7.63$, and $b=1.41$ when $2<T_c/T<7$; the value of b agrees with infrared measurements of the energy gap. This sort of analysis could not be applied to In, for below 0.8°K the total superconducting specific heat was less than the normal lattice term. A possible interpretation is that θ_0 is 9% higher in the superconducting state than in the normal metal at 0.4°K; this is not supported, however, by the recent acoustic measurements of the elastic constants by Chandrasekhar and Rayne. The anomaly is not as yet understood, but a few plausible explanations are discussed.

INTRODUCTION

RECENT theories on the electronic and lattice contributions to the specific heat of superconductors continue to stimulate measurement of their heat capacities to still lower temperatures. The BCS theory[1] resulted in a formula for the electronic specific heat which could be approximated by

$$C_{es}=a\gamma T_c\exp(-bT_c/T), \tag{1}$$

where γT is the electronic specific heat in the normal state and $a=8.5$, $b=1.44$ when $2<T_c/T<6$. Boorse[2] found that for $7<T_c/T<11$ the same expression would represent the BCS formula when $a=26$ and $b=1.62$. While the electronic term is quite different than in the normal state due to the appearance in the superconductor of an energy gap centered at the Fermi level, there has until now been no evidence of a change in the lattice term accompanying the transition to superconductivity. Chester has supported this view with a thermodynamic argument based on the isotope effect and assumption of certain similarity rules,[3] namely, that $C_{es}/\gamma T_c$ and the critical magnetic field ratio $H_c(T)/H_0$ are functions of the reduced temperature T/T_c which are independent of isotopic mass.

C_{es} is customarily deduced from the specific heat data on the following assumptions: (a) The normal and superconducting specific heats are expressible as the sum of electronic and lattice terms:

$$C_n=C_{en}+C_{ln} \tag{2a}$$

and

$$C_s=C_{es}+C_{ls}, \tag{2b}$$

excluding such additional contributions as come from the nuclei or magnetic impurities. (b) The normal electronic term has the temperature dependence characteristic of the specific heat of a degenerate Fermi gas:

$$C_{en}=(\pi^2k^2/3)N(\zeta)T=\gamma T, \tag{3}$$

where $N(E)dE$ is the number of electronic states in the energy interval dE and ζ is the Fermi energy. (c) The normal lattice term can be represented by the expansion

$$C_{ln}=\alpha T^3+\beta T^5+\mu T^7+\cdots. \tag{4}$$

The coefficient α is related to the Debye temperature θ_0 at absolute zero and the gas constant R by

$$\alpha=(12\pi^4/5)R\theta_0^{-3}. \tag{5}$$

(d) C_{en} and C_{ln} are independent of the magnetic field applied to quench superconductivity while measuring C_n below T_c. (e) The lattice term is the same in both states, i.e.,

$$C_{ls}=C_{ln}. \tag{6}$$

The electronic part of C_s is then considered to be the difference between C_s and $(C_n-\gamma T)$.

The heat capacity of indium had previously been measured by Clement and Quinnell[4] down to 1.7°K. At that temperature, C_{ln} is still three times γT and T_c/T is only 2. The present measurements extend data down to 0.35°K through the use of a helium-three cryostat,[5] and allow a more accurate determination of γ. Because of the relatively high transition temperature ($T_c=3.4$°K) and the low θ_0 of 108°K, values of T_c/T to nearly 10 could be obtained, where C_{es} is expected to be negligible compared to C_{ls} according to Eqs. (1) and (5). Thus, the measurement provided a test of the assumption expressed in Eq. (6). We recently reported the unexpected result[6] that C_s is less than C_{ln} below

* Based on part of a Ph.D. thesis submitted to the faculty of Purdue University. This work was supported by a Signal Corps contract.

† Present address: International Business Machines, Yorktown Heights, New York.
‡ On leave of absence at the Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands.

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[2] H. A. Boorse, Phys. Rev. Letters **2**, 391 (1959).
[3] G. V. Chester, Phys. Rev. **104**, 883 (1956).
[4] J. R. Clement and E. H. Quinnell, Phys. Rev. **92**, 258 (1953).
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0.8°K. This result conflicts with one or more of the above common assumptions unless one admits a negative contribution to the heat capacity. As a consequence of this behavior, it is not possible to estimate C_{es} directly from the specific heat data. A small nuclear electric quadrupole contribution is expected similar to that found in Re[7] and Bi,[8] but it is smaller than the anomalous change in C_s and could not be observed. In this paper we will present the indium results in fuller detail, together with some new data on tin.

The specific heat of tin has previously been reported by Corak and Satterthwaite[9] and Goodman[10] above 1°K and by Zavaritskii[11] also below 1°K. All of their results were consistent with the above assumptions (a) through (e) used to obtain $C_{es}(T)$. The present work on tin was primarily an effort to disclose in our measurements systematic tendencies to underestimate the heat capacity below 1°K. The resulting data could be analyzed in the customary way, and revealed no deviations such as seen in superconducting indium.

MEASUREMENT

Apparatus

The helium-three cryostat used for these measurements will maintain temperatures as low as 0.35°K in a relatively large volume for two days without warmup. Since it has been described in detail elsewhere,[5] only a few features pertaining to the reliability of the measurement need be mentioned here. The specimen is cooled by means of a mechanical heat switch in the absence of exchange gas, so that there is no heat of gas desorption contributed during a measurement. Heating is done electrically through a clock-controlled switch and the temperature recorded by means of a $\frac{1}{10}$-w, 10-ohm Allen Bradley carbon composition resistor cemented to the specimen with glyptal lacquer.

After completion of heat-capacity measurements, exchange gas is admitted to the vacuum spaces and the resistance thermometer calibrated against helium-three and helium-four vapor pressures using the helium-three scale of Sydoriak and Roberts[12] and the 1958 scale for helium-four.[13] Below 0.4°K the correction required for the thermomolecular pressure gradient is a large fraction of the measured helium-three pressure and the effect of gas viscosity becomes important, so a paramagnetic salt thermometer is used instead.[5] Between 1.0° and 1.3°K, a comparison of the helium-three and helium-four bath pressures revealed that the former was lower than should be expected. This could be explained by a contamination of the helium-three by about 1% helium-four and the assumption of Raoult's law of partial pressures. Consequently, all helium-three pressures were corrected by +1% in the calibration for indium. Before the tin measurements the helium-three was purified by fractional distillation, and no such correction was necessary thereafter.

The systematic error in specific heat due to inaccuracies in temperature scale and calibration is thought not to exceed 1% above 1°K, but may be as high as 3% at the lowest temperature. Other systematic errors in heating current, heater resistance, timing, and correction for heat capacity of the addenda total at most another percent. Graphical scatter in the data also amounts to about a percent.

Specimens

The polycrystalline tin came from the Consolidated Mining and Smelting Company of Canada, Ltd., Trail, British Columbia, who claim 99.999% purity. A 137-g piece, allowed to self-anneal at room temperature, produced results indistinguishable from a 209-g piece which was annealed in air for an hour at 200°C before mounting in the cryostat. The two indium specimens were both from a 99.99% pure polycrystalline ingot supplied by the Indium Corporation of America. One, weighing 168 g and hereafter called In I, was mounted as received, and may have been strained. The second,

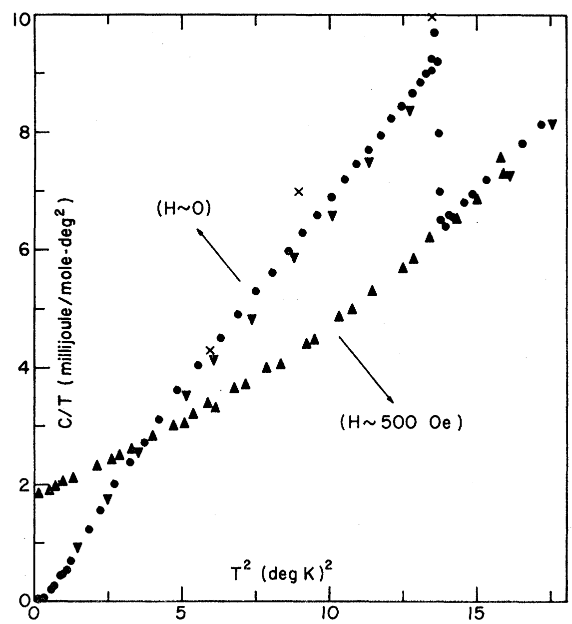

FIG. 1. Specific heat of tin in normal and superconducting states. Our data (● and ▲) are here compared with those of Corak and Satterthwaite (▼) and Zavaritskii (×).

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[12] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957). We used their temperatures which were based on the 1955*E* He^4 scale, adjusting them to the value which Sydoriak and Roberts would have obtained, had they used the 1958 He^4 scale.
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TABLE I. Specific heat of tin in normal and superconducting states. (C is in mjoule/mole deg.)

T, °K	C/T ($H=0$)	T, °K	C/T ($H\simeq 500$ oe)	T, °K	C/T ($H=0$)	T, °K	C/T ($H\simeq 500$ oe)
	Sn I				Sn II		
0.4374	0.0441	0.4026	1.83	0.4061	0.0400	0.6482	1.90
0.4449	0.0460	0.4237	1.88	0.4060	0.0386	0.7340	1.97
0.5021	0.0623	0.4374	1.83	0.4233	0.0445	0.8374	2.01
0.5084	0.0640	0.4847	1.94	0.4798	0.0585	0.9474	2.06
0.5727	0.0888	0.6042	1.87	0.5350	0.0738	1.0129	2.08
0.6274	0.1106	0.7062	1.82	0.6112	0.1090	1.0189	2.11
0.6678	0.1404	0.7319	1.92	0.7021	0.1602	1.1748	2.16
0.6874	0.1440	0.7575	1.89	0.7393	0.1799	1.3582	2.27
0.7117	0.1642	0.7975	1.95	0.9189	0.409	1.5166	2.38
0.7407	0.1876	0.8303	1.99	0.9923	0.512	1.6965	2.53
0.7712	0.215	0.9067	2.01	1.0404	0.589	1.9983	2.87
0.8047	0.247	0.9778	2.05	1.1078	0.702	2.596	3.67
0.8326	0.281	1.0329	2.04	1.2193	0.945	3.036	4.43
0.8804	0.337	1.1502	2.11	1.3571	1.240	3.383	5.33
0.9217	0.392	1.2391	2.19	1.4954	1.567	3.665	6.21
0.9630	0.456	1.3461	2.24	1.6616	2.01	3.878	6.88
1.0490	0.595	1.5163	2.35	1.9302	2.73	4.069	7.85
1.1307	0.745	1.8190	2.65	2.221	3.64	4.240	8.36
1.2069	0.900	2.161	3.02	2.511	4.53		
1.2985	1.104	2.377	3.29	2.744	5.31		
1.4172	1.382	2.555	3.56	2.938	5.99		
1.5744	1.785	2.903	4.15	3.101	6.61		
1.7272	2.19	3.170	4.71	3.244	7.20		
1.8961	2.67	3.387	5.52	3.365	7.73		
2.028	3.06	3.574	5.74	3.477	8.25		
2.138	3.40	3.874	6.69	3.579	8.68		
2.404	4.14			3.644	9.01		
2.655	5.00			3.719	6.62		
2.837	5.65			3.668	9.07		
3.007	6.33			3.678	9.22		
3.153	6.90			3.695	9.22		
3.280	7.39			3.706	7.09		
3.393	7.81			3.722	6.40		
3.495	8.26			3.737	6.69		
3.589	8.81			3.749	6.63		
3.729	6.40			3.765	6.58		
3.839	6.87			3.857	6.97		
4.154	8.13			3.986	7.56		
4.389	8.99			4.148	8.16		

In II, weighing 95 g, was cast in a high-purity graphite mold in vacuum and allowed to solidify over a period of 40 min, then cooled in 2 hr to 100°C. No impurities could be detected spectroscopically in samples from this casting. After mounting in the cryostat, it was enclosed in a can which was pumped to rough vacuum and immersed in boiling water for 6 hr.

For the heater, 1.75-mil constantan wire was wrapped around the ingots (54 cm on In and 40 cm on Sn) and cemented in place with glyptal. Because some heat escapes along the electrical leads instead of warming the specimen, the loose ends of these wires were tinned for some distance to ensure heating only of the part in good thermal contact with the ingot. The potential

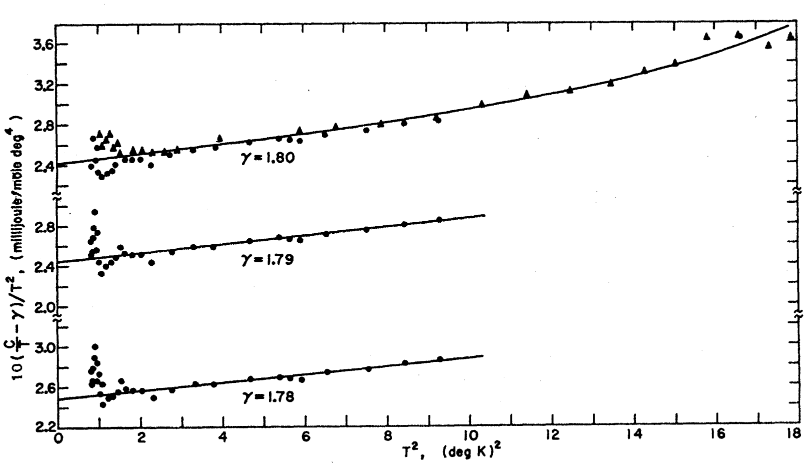

FIG. 2. Graphical determination of parameters in the specific heat of normal tin. The plot for which $\gamma = 1.80$ mjoule/mole deg^2 includes results on both specimens, and was chosen as best represented by Eqs. (2a), (3), and (4).

TABLE II. Specific heat of indium in normal and superconducting states. (C is in mjoules/mole deg.)

T (°K)	C/T ($H=0$)	T (°K)	C/T ($H\simeq 300$ oe)
	In I		
0.3704	0.167	0.4819	1.989
0.3595	0.149	0.5648	2.119
0.3447	0.138	0.6487	2.240
0.3880	0.180	0.8147	2.626
0.4447	0.238	0.8385	2.677
0.5216	0.352	0.8738	2.774
0.5892	0.443	0.9065	2.856
0.6149	0.516	0.9461	2.970
0.6607	0.601	0.9862	3.182
0.7291	0.765	1.0381	3.235
0.7849	0.938	1.0874	3.413
0.6538	0.828	1.1434	3.597
0.7959	0.968	1.1073	3.442
0.8556	1.162	1.1819	3.712
0.9069	1.347	1.3376	4.348
0.9728	1.620	1.4496	4.863
1.0707	2.017	1.6068	5.607
1.1792	2.563	1.9523	7.567
1.2884	3.136	2.482	11.29
1.4498	4.129	2.829	14.10
1.7136	5.904	3.417	19.93
2.0717	8.652		
2.6711	14.27		
2.888	16.50		
3.188	20.10		
3.442	20.52		
3.549	21.63		
3.849	25.39		
4.105	29.05		
3.121	19.38		
3.220	20.51		
3.310	21.68		
	In II		
0.3789	0.162	0.3669	1.788
0.4137	0.199	0.4197	1.904
0.4571	0.250	0.4754	1.962
0.5299	0.350	0.5534	2.058
0.6172	0.487	0.6344	2.204
0.6753	0.614	0.6623	2.253
0.7059	0.690	0.7089	2.331
0.7389	0.757	0.7498	2.425
0.8216	0.996	0.8048	2.537
0.8800	1.202	0.8676	2.697
0.9578	1.509	0.9511	2.963
1.0370	1.884	1.0896	3.416
1.0294	1.839	1.2002	3.805
1.1558	2.456	1.3609	4.452
1.3493	3.535	1.5481	5.348
1.5551	4.829	1.6931	6.094
1.6744	5.670	1.8628	7.050
1.8956	7.350	2.1481	8.802
2.2516	10.41	2.472	11.21
2.594	13.66	3.029	16.07
2.833	16.23	3.551	21.59
3.020	18.36	4.154	29.26
3.251	21.02	4.658	36.59
3.451	20.68		
3.576	22.20		

leads to heater and thermometer were of the same constantan wire. For In I, the current leads were all of niobium welded to nickel at the ends, which were in turn soldered to the terminals. Since it was feared that too much heat might develop in the welded contacts, the heater current leads were replaced by 50-gauge copper wire for In II and tin.

RESULTS

Tin

Representative specific heat data on tin are listed in Table I and plotted as C/T against T^2 in Fig. 1 along with the results of Corak and Satterthwaite,[9] Goodman,[10] and Zavaritskii.[11] The upward curvature of the normal-state data indicates the presence of at least a T^5 term in the lattice contribution. For deciding values of the parameters in Eqs. (3) and (4) which would best fit the data, $(C_n-\gamma T)/T^3$ is plotted against T^2 in Fig. 2. The points at lowest temperatures are most affected by the choice of γ, and that γ has been chosen for which these points fall most nearly on a straight line. The ordinate of this line at $T^2=0$ is α, and its initial slope is β. The upward curvature in this plot indicates the need of a T^7 term in representing the lattice contribution, so the normal specific heat becomes

$$C_n=(1.80\pm0.02)T+(0.242\pm0.01)T^3+0.0040T^5 +0.00014T^7 \text{ mjoule/mole deg.} \quad (7)$$

Only the statistical errors are given here. According to Eq. (5) the Debye temperature is 200±3°K. Rayne and Chandrasekhar have measured the elastic constants of tin,[14] and from them calculated the value of θ_0 to be 201.6±2.6°K.

Superconducting Electronic Term

Figure 3 is a detail of Fig. 1 below 0.9°K in which the solid line through the origin represents $(\alpha T^3/T)$, the

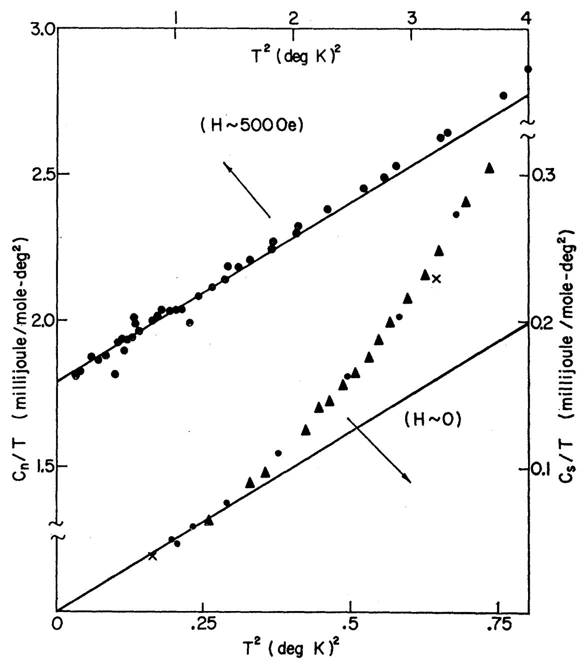

FIG. 3. Detail of the specific heat of tin below 1°K. A solid line through the origin represents the normal lattice term.

[14] J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. 120, 1658 (1960).

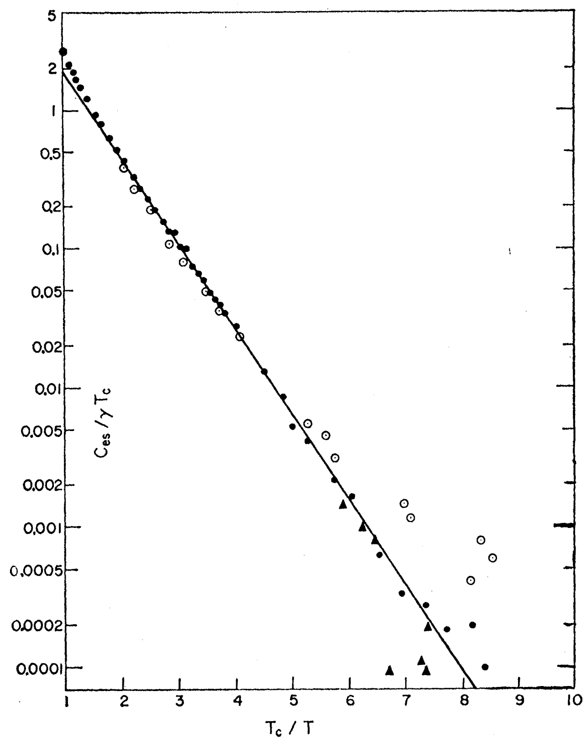

FIG. 4. Electronic specific heat of superconducting tin. The present data are represented by Eq. (1) when $2<T_c/T<7$. Goodman's results are the open circles.

dominant lattice term in this region. Data for the superconducting state ($H=0$) appear to approach this line asymptotically as C_{es} dies out at very low temperatures. To test whether C_{es} is an exponential function, $C_s-(C_n-\gamma T)$ is plotted semilogarithmically against T_c/T in Fig. 4. For values of T_c/T between 2 and 7, the points are indeed represented by Eq. (1) with $T_c=3.70$°K, $a=7.63$, and $b=1.41$; uncertainties do not permit evaluation of C_{es} beyond this range. The BCS theory[1] yields an energy gap at 0°K of $3.50kT_c$ corresponding to $b=1.44$. Following Goodman, we may evaluate the specific heat energy gap in Sn as

$$(1.41/1.44)(3.50kT_c)=3.43kT_c.$$

This compares favorably with $(3.3\pm0.2)kT_c$ found by Ginsburg and Tinkham and $(3.6\pm0.2)kT_c$ by Richards and Tinkham, both from infrared absorption measurements.[15]

Transition Temperature

The midpoint of the specific heat discontinuity occurred at 3.701°K, and this temperature is regarded as T_c. This is considerably lower than the 3.713°K reported by Corak and Satterthwaite[9] (corrected to the 1958 temperature scale) and 3.722°K from the magnetic measurements of Shaw, Mapother, and Hopkins.[16] To determine whether some property of the tin was responsible for this difference, a small piece was cooled inside a set of coils immersed in liquid helium. The temperature at which the mutual inductance of the coils was halfway through its change, 3.714°K, is T_c in the earth's field. Corrected to zero field, it would be 3.718°K, about midway between the values reported in references 9 and 16. Although a Helmholtz coil was set up to cancel the earth's field to within 0.1 oe during the heat-capacity measurements, it is believed that magnetic flux can have been trapped by layers of superconducting solder near the specimen. However, the intensity would have to have been four times the earth's field to explain the observed difference. It is believed that positive changes in T_c of up to 0.1°K can result from strains introduced on cooling because of anisotropic contraction.[17] If our bulk material had been strained in such a way as to depress T_c, perhaps the small piece from the surface was not, and this would account for the difference.

Calculation of Threshold Field

The critical magnetic field intensity $H_c(T)$ at which the normal and superconducting phases are in equilibrium at the temperature T is related thermodynamically to the specific heats by

$$(V_m/8\pi)[H_c(T)]^2=\int_{T_c}^{T}d\tau\int_0^{\tau}dT(C_s-C_n)/T \quad (8)$$

where V_m is the molar volume. The entropy difference at T_c, $\int_0^{T_c}dT(C_s-C_n)/T$, was not significantly different from zero, as should be expected for a second order transition. Figure 5 shows the deviation of $H_c(T)$ from a parabolic temperature dependence, $D(T^2/T_c^2)=D(t^2)=1-t^2-H_c(T)/H_0$, calculated from the specific

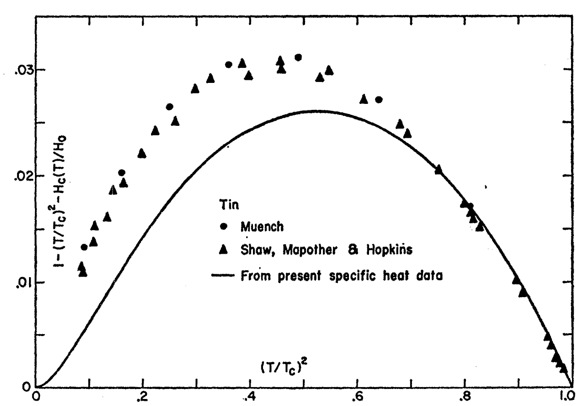

FIG. 5. Deviation of the critical magnetic field in tin from a parabolic temperature dependence.

[15] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

[16] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

[17] T. E. Faber, Proc. Roy. Soc. (London) **A241**, 545 (1957).

TABLE III. Results of measurements on tin and indium.

Measurement	Temp. range (°K)	γ(mjoule/mole deg^2)	θ_0 (deg K)	β (mjoule/mole deg^6)	a	b	T_c, °K (1958 scale)	H_0 (oe)	$-(dH_c/dT)_{T_c}$ (oe/deg)
Tin I & II	0.4–4.2	1.80±0.02	200 ±3	0.004	7.63	1.41	3.701	306	149±6
Corak and Satterthwaite[9]	1.2–4.5	1.75±0.01	195.0±0.6		9.2	1.50	3.722	303.4	
Rayne and Chandrasekhar (acoustic)[14]	4.2–300	1.76[a]	201.6±2.6	0.005[a]	10.03[a]	1.53[a]			
Zavaritskii[11]	0.15–4		202 ±3			1.35		301±6	
Muench[18]	1–3.7						3.728±0.002	307.3	147±1
Shaw, Mapother, and Hopkins[16]	1–3.7						3.722	308.7	
In I	0.35–4.2	1.61±0.02	109 ±1	0.008	11[a]	1.6[a]	3.403[a]	284	156[a]
In II	0.35–4.2	1.59±0.02	108 ±1	0.008	11[a]	1.6[a]	3.403[a]	284	156[a]
Clement and Quinnell[4]	1.7–21.3	1.81	109 ±0.3				3.387	278.4[a]	
Chandrasekhar and Rayne (acoustic)[24]	1.4–4	1.65[a]	111.3±1						
Muench[18]	1–3.4						3.412±0.003	284.5	156±1
Reeber[22]	1–3.4						3.407±0.002	293	156
Shaw, Mapother, and Hopkins[16]	1–3.4						3.408	285.7	

[a] Calculated or estimated from other data.

heat. Resulting values of H_0 and $(dH_c/dT)_{T_c}$ are listed in Table III along with values from the magnetic measurements of Muench[18] and Shaw, Mapother, and Hopkins.[16]

Indium

Nuclear Term

Before analysis of the indium data, some of which appear in Table II, a nuclear electric quadrupole contribution was deducted from the specific heat. The nuclei of both natural isotopes have spin $I=9/2$ and are distributed among five doubly degenerate energy levels determined by interaction of the nuclear electric quadrupole moment and the axially symmetric electric field gradient at the nucleus. These energy levels are given by[19]

$$E_m=A'[3m^2-I(I+1)],\quad m=\tfrac{1}{2},\tfrac{3}{2},\cdots,9/2, \tag{9}$$

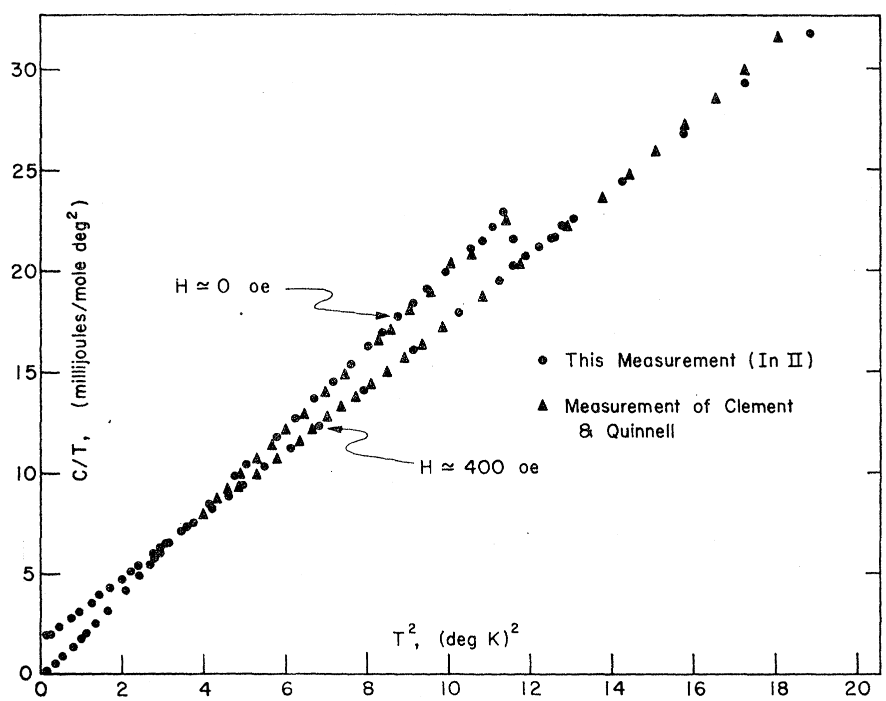

FIG. 6. Specific heat of indium in normal and superconducting states.

[18] N. L. Muench, Phys. Rev. 99, 1814 (1955).
[19] T. P. Das and E. L. Hahn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Suppl. 1.

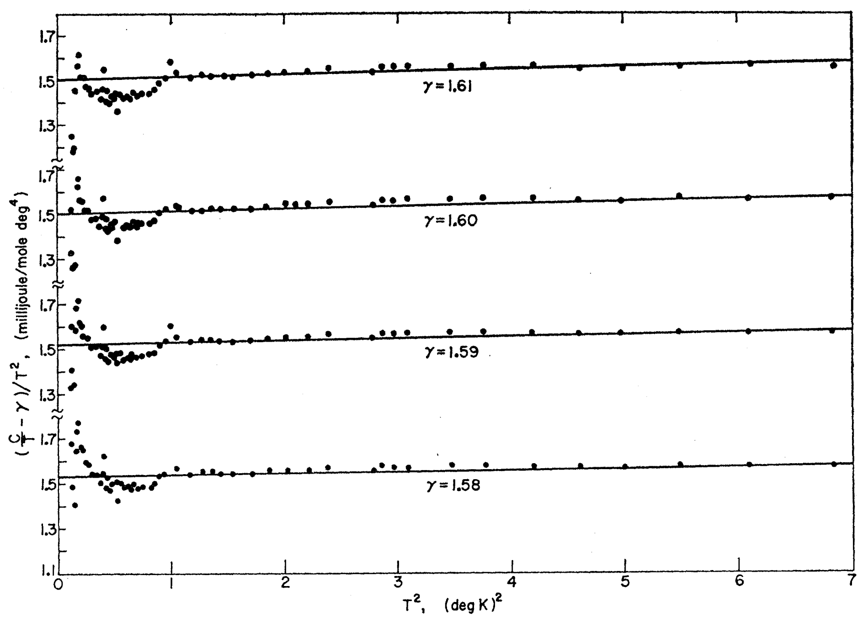

FIG. 7. Graphical determination of parameters in the specific heat of normal indium. This figure shows the In II data, for which $\gamma=1.59$ mjoule/mole deg^2 was chosen.

where $mh/2\pi$ is the component of the nuclear angular momentum along the symmetry axis of the crystal and $A'=e^2qQ/4I(2I-1)$. The product of the scalar quadrupole moment eQ and the maximum electric field gradient at the nucleus, eq, is the coupling constant for the interaction, and has been measured by Hewitt and Knight using an rf resonance technique.[20] Their results give for the average coupling constant, weighted according to natural abundance of In^{113} and In^{115}, h(45.21 Mc/sec). A standard statistical calculation results in the nuclear specific heat,

$$C_q=(66/5)Ra^2T^{-2}, \tag{10}$$

in the high-temperature approximation where $T\gg a=6A'/k$. From the value of the coupling constant it follows that $a=9.04\times10^{-5}$ °K and $C_q=8.97\times10^{-4}\ T^{-2}$ mjoule/mole deg. At 0.35°K, C_q is only 11% of C_s and falls below 1% of C_s above 0.6°K. No such nuclear term was expected in tin because all naturally occurring isotopes have I either $\frac{1}{2}$ or 0, and consequently E_m is a singlet or a degenerate doublet.

Normal State

It was then assumed that C_q was not changed appreciably by the applied magnetic field and (C_n-C_q) was analyzed by a procedure analogous to the one used to obtain C_n for tin. From Figs. 6 and 7 it was found that

$$(C_n-C_q)=(1.59\pm0.03)T+(1.53\pm0.03)T^3+0.008T^5 \tag{11}$$

represented the In II data and from similar graphs that

$$(C_n-C_q)=(1.61\pm0.03)T+(1.50\pm0.03)T^3+0.008T^5 \tag{12}$$

mjoule/mole deg represented the In I data over the entire temperature range of the measurement. The errors quoted are graphical uncertainties only.

Superconducting State

In Fig. 8, a straight line of slope $\alpha=1.5$ mjoule/mole deg^4 has been drawn through the origin to represent the normal lattice term. In contrast to tin, the points taken

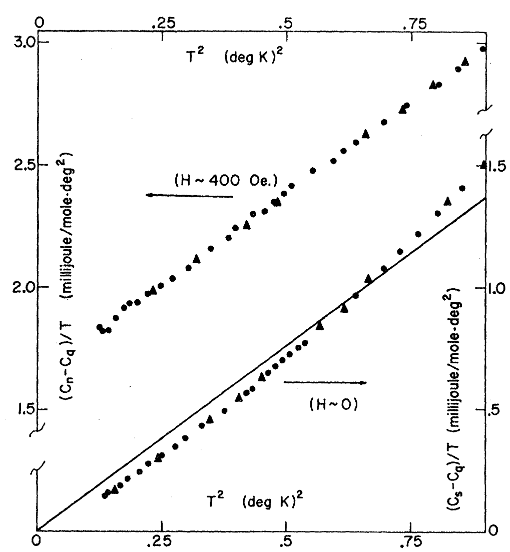

FIG. 8. Detail of the specific heat of In I and In II below 1°K. A solid line through the origin represents the normal lattice term.

[20] R. R. Hewitt and W. D. Knight, Phys. Rev. Letters 3, 18 (1959).

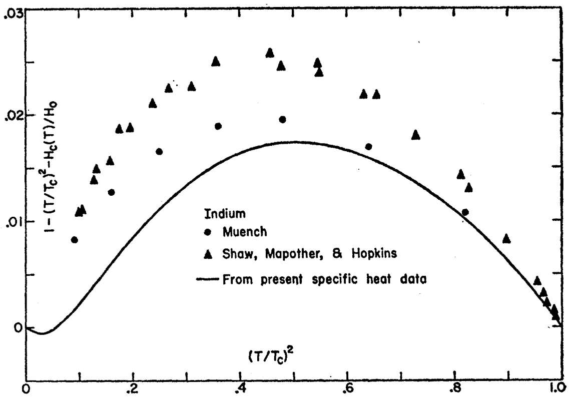

FIG. 9. Deviation of the critical magnetic field in indium from a parabolic temperature dependence.

in zero field fall well below the line so that for $T<0.6°$K, (C_s-C_q) is less than the normal lattice term. By assuming values for a and b in Eq. (1), one can estimate C_{es} and fit analytic expressions to the remaining part of (C_s-C_q). From values of a and b for other superconductors and data on the energy gap,[15] the best numbers appear to be $a=11$ and $b=1.6$ for indium; below 1°K, C_{es} is less than 20% of the total, so that a large error in the estimate is tolerable. Regarding the rest of (C_s-C_q) as a modified T^3 lattice term, we find, in the customary units:

$$(C_s-C_q-C_{es})=1.78\exp(-0.059T_c/T)T^3 \quad (13a)$$

for In I and

$$(C_s-C_q-C_{es})=1.72\exp(-0.051T_c/T)T^3 \quad (13b)$$

for In II, when $2<T_c/T<10$. Taking an alternate point of view, that the lattice term is unchanged but there is a negative term of unknown origin, we find:

$$(C_s-C_q-C_{es})=1.50T^3-0.12T^{1.6}, \quad 0.35<T<0.7°\mathrm{K} \quad (14a)$$

for In I and

$$(C_s-C_q-C_{es})=1.53T^3-0.16T^{1.9}, \quad 0.35<T<0.85°\mathrm{K} \quad (14b)$$

for In II.

Threshold Magnetic Field

For the purpose of calculating the critical field according to Eq. (8), lines were fit to a large scale plot of C/T against T for both In I and In II such as to satisfy the following conditions: (a) In those regions where the results were different for the two specimens (by as much as 2% just below T_c in the superconducting state), the lines were drawn somewhere between the two sets of points. (b) The transition was considered to be a sharp discontinuity at $T_c=3.403°$K. (c) The difference in specific heats at T_c given by Rutgers' formula,

$$(C_s-C_n)_{T_c}=(V_mT_c/4\pi)[(dH_c/dT)^2]_{T_c}, \quad (15)$$

was made to agree with the result of Muench[18] that $(dH_c/dT)_{T_c}=156$ oe/deg using Swenson's value for the molar volume V_m at absolute zero,[21] 15.37 cm^3/mole. This requirement was consistent with the first condition. (d) The lines were then adjusted where the fit was uncertain so as to make the entropy difference $\int_0^{T_c}dT(C_s-C_n)/T$ equal to zero. The resulting deviation curve (Fig. 9) is exceptional in that the deviation $D(t^2)$ changes sign; this has never been observed in a critical-field measurement. The initial slope of this curve at $t^2=0$ is

$$D'(t^2)=(2\pi\gamma/V_m)(T_c/H_0)^2-1, \quad (16)$$

which depends on the choice of γ; for a positive initial slope, we would need $\gamma=1.70$ mjoule/mole deg^2. The specific heats give $H_0=284$ oe, while Muench[18] found 284.5; Reeber,[22] 293; and Shaw, Mapother, and Hopkins,[16] 285.7±0.5 oe.

DISCUSSION

We exclude systematic errors in the measurement as important contributions to the In anomaly. The errors, as well as the nuclear contribution estimate, are several times smaller than the deviation in C_s, which is as much as 30% below C_{ln}. A similar deviation has been observed in niobium by Boorse, Hirschfield, and Leupold,[23] who recently reported a $C_s(T)$ which was lower than the normal lattice term below $T_c/5$. Their measurements extended down to 1.1°K, or about $T_c/8$, where θ_0 in the superconducting state was estimated to be 5% higher than in the normal state.

Assuming that C_s in indium is almost entirely in the lattice at the lowest temperature, its value corresponds to $\theta_0=121°$K as compared with 109°K in the normal state. This result demanded careful measurement of the elastic constants, which Chandrasekhar and Rayne have just performed down to 1.4°K.[24] By observing a distant echo of a pulse of 10-Mc/sec acoustic waves in an oriented single In crystal, they could detect a change in transit time of one part in 2×10^4. At no temperature did they observe a detectable difference of transit time in the normal and superconducting states; θ_0 was calculated to be 111.3±1°K for both. By fitting the expression

$$C_n=C_q+(12\pi^4/5)R(T/\theta_0)^3+\gamma T, \quad (17)$$

to our data below 0.7°K and using their θ_0, they found $\gamma=1.65$ mjoule/mole deg^2.

[21] C. A. Swenson, Phys. Rev. **100**, 1607 (1955).
[22] M. D. Reeber, Phys. Rev. Letters **4**, 198 (1960).
[23] H. A. Boorse, A. T. Hirschfield, and H. Leupold, Phys. Rev. Letters **5**, 246 (1960).
[24] B. S. Chandrasekhar and J. A. Rayne, Phys. Rev. Letters **6**, 3 (1961). David and Blangé have recently communicated to us results of similar experiments.

The acoustic and heat capacity measurements are not necessarily conflicting. The 10-Mc/sec phonons have very long wavelengths, the order of 3×10^{-2} cm, while at $\frac{1}{3}$°K, the kT phonons are only about 4×10^{-5} cm long. The coherence distance of the attractive electron-electron interaction giving rise to superconductivity[1] is the order of 10^{-4} cm. We need a quite special mechanism, operating in these two superconductors, which causes stiffening of the lattice (or an increase in the elastic constants) in the superconducting state, but only for short-wave phonons, or perhaps only for those wavelengths near the coherence distance.

From the point of view of a two-fluid model, one can regard the lattice in the normal state as vibrating in a viscous medium, the electron gas. As T drops below the transition temperature, the superfluid fraction increases rapidly; corresponding to the decrease in viscosity of the electrons is an increase in frequencies, and hence energies, of the normal lattice modes. The result is a lowered heat capacity. The exponential factor in the empirical expressions (13) favors somewhat this point of view. It is interesting to estimate the effect on the heat capacity of changes in the zero-point energy, which on the Debye model of a lattice is given by

$$3N\int_0^{\nu_{\max}} d\nu\,\tfrac{1}{2}h\nu A\nu^2 \Big/ \int_0^{\nu_{\max}} d\nu\, A\nu^2 = \frac{9R\theta_D}{8}. \quad (18)$$

Assuming that the temperature dependence of this quantity is due solely to an increase in the cutoff frequency $\nu_{\max}$ toward lower temperatures in the superconducting state, there results a negative specific heat contribution $(9R/8)d\theta_D/dT$. At 0.4°K, C_{ls} is 30% below the value it would have been, had θ_D remained constant, corresponding to $(d\theta_D/dT)\simeq-0.3(\alpha/R)\times(0.4°\mathrm{K})^3\simeq-5\times10^{-6}$. A small temperature dependence of the high-frequency cutoff affects the ground state of a large number of normal modes, resulting in a significant change in the specific heat. BCS[1] have calculated that the shift in lattice zero-point energy during the superconducting transition is the order of a thousandth of the electron condensation energy, W_0. Their estimate gives

$$W_0\simeq N(0)(kT_c)^2=3\gamma(T_c/\pi)^2\simeq6 \text{ mjoule/mole}, \quad (19)$$

or a shift in the zero-point energy of the In lattice by a few microjoules per mole. This energy shift is much smaller than would be estimated from the apparent difference in lattice terms, $\int_0^{T_c}(C_{ln}-C_{ls})dT$. Another difficulty with this approach is that the depression of C_{ls} depends on $d\theta_D/dT$, and hence, the rate at which the superfluid density changes. The change is greatest just below T_c, and hence the depression of C_{ls} should
just below T_c, and hence the depression of C_{ls} should
be far greater there than the lowest temperatures, where θ_D should be more nearly constant. The former interpretation, in which C_{ls} depends on the density of superfluid rather than on its temperature derivative, is more satisfying.

There seems to be no feature common to In and Nb which distinguishes them from Sn and other elements[2] for which C_{es} has been determined well below T_c. The In lattice is face-centered tetragonal and Nb is body-centered cubic, while Sn is double body-centered tetragonal. In has a very low θ_0 and θ_0/T_c, but the values of these parameters for Sn are lower than for Nb. Perhaps the essential feature lies in the electronic distribution. Jones has calculated a contribution to the specific heat which arises from the effect of thermal electronic excitation on the shear constant c_{44}.[25] The specific heat term is $\beta E_0T\partial^2\ln c_{44}/\partial T^2$, where β is a constant the order of 1 and E_0 is the lattice zero-point energy. The free energy W involves a parameter p which is defined as the distance from the origin to a face of the Brillouin zone. The temperature dependence of c_{44} is then calculated from

$$c_{44}=(4/9)p^2\partial^2(W/\Omega)/\partial p^2+(8/9)p\partial(W/\Omega)/\partial p, \quad (20)$$

with the help of assumptions on the p dependence of W; Ω is the atomic volume. The contribution is significant only when the Fermi surface lies close to the Brillouin zone boundaries, so that its contour is sensitive to p. In the model of a normal metal (the α brasses) which Jones considered, it is positive and proportional to T (W is proportional to T^2). But in the superconducting state, with an energy gap centered at the Fermi surface and W having an exponential T dependence, one would expect Jones' specific heat term to be exponential in character. Its sign and magnitude would depend on the details of energy surfaces near the zone boundaries and their sensitivity to p, i.e., to shear strain of the lattice. However, it is not clear how this theory can lead to a change in the elastic constants during the superconducting transition and at the same time explain the negative result of acoustic measurements.

ACKNOWLEDGMENTS

The authors are grateful to Miss Louise Roth for preparing the specimens and to A. G. Sadasiv and B. J. C. van der Hoeven for valuable assistance with the measurements. We acknowledge several stimulating discussions with Dr. S. Rodriguez and Dr. A. R. de Vroomen. One of us (C. A. B.) is grateful to the National Science Foundation for support during the progress of this work.

[25] H. Jones, Proc. Roy. Soc. (London) **A240**, 321 (1957).
[25] H. Jones, Proc. Roy. Soc. (London) **A240**, 321 (1957).