

lattice in general, and (iii) the Jahn-Teller effect. The results of his calculations based on a dipole model for the trigonal field give a total splitting from all three sources of  $1075\text{ cm}^{-1}$  of which  $550\text{ cm}^{-1}$  is due to a Jahn-Teller effect.<sup>16</sup> This work of Val Vleck is interesting not only because his prediction of the energy level splitting closely approximates the values calculated in this paper, but also because of the implication of the Jahn-Teller effect. In one of his papers,<sup>15</sup> he points out that a linear combination of tetragonal and trigonal types of distortion could produce a lower energy than either acting alone. The suggestion being made here is that such a Jahn-Teller distortion, which would be less than axially symmetric, could account for the observed

<sup>16</sup> J. H. Van Vleck, *Phys. Rev.* **57**, 435 (1940).

crystal field symmetry of  $\text{Ti}^{3+}$  ions in  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . However, since there is no direct evidence of this effect and ample reason to expect an additional ligand displacement because  $\text{Ti}^{3+}$  is a larger ion ( $0.76\text{ \AA}$ ) substituted for a smaller  $\text{Al}^{3+}$  ion ( $0.51\text{ \AA}$ ), a Jahn-Teller effect in this material must remain in the realm of speculation.

#### ACKNOWLEDGMENTS

The author wishes to thank Professor G. A. Woonton for his interest and encouragement during the course of this work. Gratitude must also be expressed to the National Research Council for awarding a studentship to the author during his resident studies at McGill University. The research was supported by the Defense Research Board through grant DRB 9512-20.

## Low-Temperature Heat Capacities of Indium and Tin\*

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The heat capacity of indium has been measured between 0.08 and  $4.2^\circ\text{K}$  in the normal state ( $H = 1000\text{ Oe}$ ) and between  $0.1^\circ\text{K}$  and the critical temperature in the superconducting state. At  $T \leq 0.8^\circ\text{K}$ ,  $C_n = 0.00101T^{-2} + 1.69T + 1.42T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$  and at  $T \leq 0.35^\circ\text{K}$ ,  $C_s = 1.22T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$ . The absence of the hyperfine contribution to  $C_s$  is a consequence of the long spin-lattice relaxation time. Below  $0.35^\circ\text{K}$ , where the superconducting-state lattice heat capacity can be measured, the normal-state lattice heat capacity is only a small part of  $C_n$  and calorimetric measurements alone cannot exclude the possibility that the lattice heat capacities in the two states are equal. However, the excellent agreement between the elastic constants and the apparent normal-state lattice heat capacity supports the conclusion that they are not. The apparent discrepancy in the lattice heat capacities is less than that reported by Bryant and Keesom but the difference is largely accounted for by differences in analysis of the normal-state data and by their assumption that the measured  $C_s$  included the nuclear quadrupole term. The measurements of  $C_s$  extend to temperatures well below that at which the electronic contribution becomes negligible and therefore permit a comparison with theoretical studies of the superconducting-state lattice heat capacity. The heat capacity of tin was measured only below  $1^\circ\text{K}$ . Below  $0.45^\circ\text{K}$ ,  $C_s = 0.246T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$ , in good agreement with the elastic constants. Within the experimental error,  $C_n = 1.78T + 0.246T^3\text{ mJ mole}^{-1}\text{ deg}^{-1}$ .

### I. INTRODUCTION

PRIOR to the report by Bryant and Keesom on the heat capacity of indium,<sup>1,2</sup> the heat capacity of superconducting metals had generally been interpreted as the sum of separable electronic and lattice contributions, the latter of which was assumed to be unchanged by the superconducting transition. This interpretation

can be summarized by the equations

$$C_n = \gamma T + C_{ln}, \quad (1)$$

$$C_s = C_{es} + C_{ls}, \quad (2)$$

and

$$C_{ln} = C_{ls}, \quad (3)$$

in which  $C_n$  and  $C_s$  are the heat capacities in the normal and superconducting states,  $C_{ln}$  and  $C_{ls}$  are the lattice contributions,  $C_{es}$  is the superconducting-state electronic heat capacity, and the electronic heat capacity in the normal state is the product of the constant  $\gamma$  and the temperature  $T$ . At low temperatures the lattice heat capacity can be expressed as a series in odd powers of  $T$ . The first term is the  $T^3$  term and its coefficient is

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<sup>1</sup> C. A. Bryant and P. H. Keesom, *Phys. Rev. Letters* **4**, 460 (1960).

<sup>2</sup> C. A. Bryant and P. H. Keesom, *Phys. Rev.* **123**, 491 (1961).

related to the Debye characteristic temperature  $\theta_0$ . For the normal state,

$$C_{ln} = \alpha_n T^3 + \beta_n T^5 + \dots, \quad (4)$$

and

$$\alpha_n = (12/5)\pi^4 R \theta_0^{-3}; \quad (5)$$

for the superconducting state analogous relations can be written. Equation (3) is then equivalent to  $\alpha_n = \alpha_s$ ,  $\beta_n = \beta_s$ , etc. Since the BCS theory<sup>3</sup> predicts that  $C_{es}$  goes to zero exponentially as  $T$  goes to zero, measurements at sufficiently low temperatures should reveal a  $T^3$  term in  $C_s$  that is equal to the one found by the conventional analysis of  $C_n$ . Bryant and Keesom made heat-capacity measurements on indium from above the transition temperature  $T_c = 3.4^\circ\text{K}$  to  $0.35^\circ\text{K}$  and interpreted their data as showing  $C_{ln}/C_{ls} \approx 1.41$  for the lowest temperature points. This result is contrary to what had been inferred from several kinds of evidence. For example, the very small size of the change in elastic constants<sup>4</sup> at the transition suggests that  $C_{ls}$  and  $C_{ln}$  should differ by no more than about 1 in  $10^4$ . Furthermore, the BCS theory, which has been so successful in explaining many of the properties of the superconducting state, treats the change in the phonon spectrum as negligible.

We have made new heat-capacity measurements on indium to confirm the existence of the effect reported by Bryant and Keesom and to extend the measurements to lower temperatures in the hope of gaining some insight into its origin. For comparison we have also made measurements on tin, which was reported by Bryant and Keesom to behave in the expected way; i.e., in accordance with Eqs. (1), (2), and (3). A preliminary report on the indium measurements has already been given.<sup>5</sup>

## II. APPARATUS

The apparatus used below  $1^\circ\text{K}$ , and shown in Fig. 1, was a modification of that described in connection with earlier experiments.<sup>6</sup> Copper potassium sulfate was retained as the cooling salt but a spherical crystal of cerium magnesium nitrate (CMN) was added to serve as the basis for the temperature measurements. Experiments by Daniels and Robinson<sup>7</sup> show that the magnetic susceptibility of CMN follows a Curie law at the temperatures of interest here. This can also be predicted from the weakness of the interactions between the ions and the absence of Stark splitting.<sup>8</sup> The mutual induc-

<sup>3</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

<sup>4</sup> B. S. Chandrasekhar and J. A. Rayne, *Phys. Rev. Letters* **6**, 3 (1961).

<sup>5</sup> H. R. O'Neal, N. M. Senozan, and N. E. Phillips, in *Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, 1963).

<sup>6</sup> N. E. Phillips, *Phys. Rev.* **114**, 676 (1959).

<sup>7</sup> J. M. Daniels and F. N. H. Robinson, *Phil. Mag.* **44**, 630 (1953).

<sup>8</sup> A. H. Cooke, H. J. Duffus, and W. P. Wolf, *Phil. Mag.* **44**, 623 (1953).

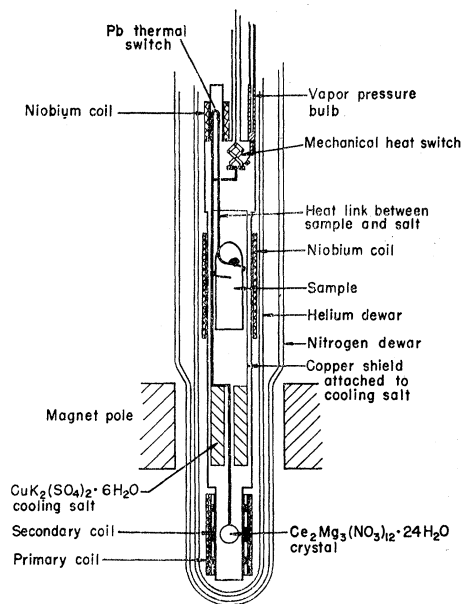


FIG. 1. The apparatus.

tance of the coils surrounding the CMN crystal was therefore assumed to be linear in  $T^{-1}$  and was calibrated against the vapor pressure of liquid He<sup>4</sup> on the 1958 He<sup>4</sup> vapor pressure scale.<sup>9</sup> Above the  $\lambda$  point, a vapor pressure bulb was used; below the  $\lambda$  point, the pressure over the bath was measured. A carbon thermometer attached to the sample and calibrated against the CMN crystal was used in the heat capacity determinations.

A copper heat link, interrupted by a lead thermal switch, was attached to the sample and to the CMN crystal with Ge 7031 varnish. The time necessary for thermal equilibrium between the sample and the CMN crystal was less than 1 min at temperatures above  $0.08^\circ\text{K}$  (the lowest temperature at which tests were made) although equilibrium with the cooling salt required appreciably longer times at the lower temperatures. Care was taken to ensure that the heat leak down electrical leads and support threads did not set up temperature differences between the sample and the CMN crystal.

In earlier apparatus the coils for applying magnetic fields to the thermal switch and to the sample were located in the liquid-nitrogen bath. The power dissipation in the coils increased the rate of boiling of the nitrogen bath, and the accompanying increase in vibration heating of the sample was a possible source of error in calibration of the resistance thermometer. In addition, the stray field of the thermal switch coil produced eddy-current heating in the sample when the switch was operated. The first of these effects was eliminated; and the second was reduced by using smaller,

<sup>9</sup> F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, *J. Res. Natl. Bur. Std. (U. S.) A64*, 1 (1960).

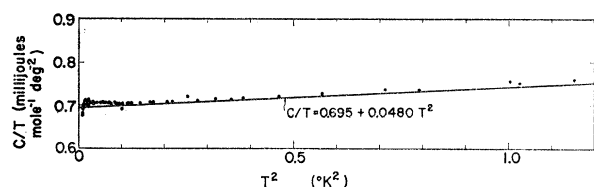


FIG. 2. The heat capacity of copper: 0.1 to 1°K. The straight line is an extrapolation from measurements above 1°K on the same sample.

superconducting coils located in the liquid-helium bath and by compensating for the dipole term in the stray field of the thermal-switch coil.

A disadvantage of the use of the superconducting coil around the sample is the small field that remains "frozen in" once the coil has been exposed to a magnetic field or used to produce one. Because of this field it is impossible to make zero-field measurements below 1°K with the coil in place. The first superconducting-state measurements were made with this coil in place and were several percent higher in the region above 0.4°K than points taken with the coil removed. This discrepancy was apparently produced by the absorption of heat accompanying a gradual transition of part of the sample to the normal state when a magnetic field was present. The superconducting-state data reported here were obtained with the coil removed and the laboratory stray field compensated.

The apparatus used above 1°K was similar to that described earlier<sup>6</sup> except for the superconducting coil used to apply a magnetic field to the sample. In order to avoid the difficulty mentioned above, the superconducting state measurements were made before the normal state measurements.

As a test of the accuracy of the measurements below 1°K, the heat capacity of a 99.999% copper sample was measured. In Fig. 2, the results are compared with an extrapolation of the heat capacity of the same sample<sup>10</sup> from above 1°K. Except at the lowest temperatures, the experimental points are systematically high but within 1% of the expected values. This discrepancy is about what might be expected to arise from the various errors in the temperature calibration of the CMN crystal. Near 0.1°K there is a large error, about 1.5%, which is probably a consequence of the uncertainty in the temperature coefficient of the resistance thermometer at the end of its range of calibration. The precision of measurements in this apparatus is usually about 1% in the adiabatic demagnetization region and somewhat better in the liquid helium region. However, for the measurements in the superconducting state near 0.1°K, the small size of the measured heat capacity reduces both the accuracy and the precision. Both samples have heat capacities of the order of 100 erg/deg in the superconducting state at 0.1°K and the correction for the

heat capacity of the addenda could introduce a systematic error of 2 or 3%. The precision is limited by fluctuations in the stray heat input to the samples: A temperature increment of  $\Delta T = T/10$  requires a heat input of 1 erg and a stray heat input of only 0.01 erg would produce an error of 1% in a heat-capacity point.

### III. HEAT CAPACITY OF INDIUM

#### A. Experimental Results

The material used in the sample was 99.999% indium supplied by the American Smelting and Refining Company.<sup>11</sup> The measurements were made on a 706-g vacuum-cast single crystal. The experimental points are given in Tables I and II and in Fig. 3.

#### B. Analysis of Normal-State Data

The normal-state heat capacity includes a hyperfine contribution,  $C_h = AT^{-2}$ , and if we retain only the first two terms of Eq. (4) the expected temperature dependence of  $C_n$  becomes

$$C_n = AT^{-2} + \gamma T + \alpha_n T^3 + \beta_n T^5. \quad (6)$$

A plot of  $C_n T^2$  versus  $T^3$  for the lowest-temperature points, shown in Fig. 4, gave  $A = 1.01 \times 10^{-3}$  mJ mole<sup>-1</sup>

TABLE I. The heat capacity of indium:  $H = 0$ . The units of heat capacity are mJ mole<sup>-1</sup> deg<sup>-1</sup>.

$T$	$C$	$T$	$C$	$T$	$C$
0.1051	0.00258	0.2113	0.01368	0.4006	0.08360
0.1064	0.00310	0.2130	0.01424	0.4175	0.09425
0.1131	0.00298	0.2329	0.01788	0.4388	0.1094
0.1149	0.00334	0.2385	0.01901	0.4543	0.1234
0.1168	0.00366	0.2506	0.02174	0.4766	0.1440
0.1175	0.00343	0.2581	0.02374	0.4932	0.1605
0.1329	0.00452	0.2610	0.02431	0.5191	0.1852
0.1407	0.00504	0.2708	0.02729	0.5223	0.1905
0.1412	0.00508	0.2808	0.02992	0.5091	0.1735
0.1422	0.00527	0.2834	0.03082	0.5604	0.2338
0.1515	0.00590	0.2876	0.03224	0.5633	0.2407
0.1524	0.00596	0.3066	0.03860	0.6183	0.3240
0.1603	0.00674	0.3178	0.04286	0.6647	0.4182
0.1608	0.00666	0.3494	0.05667	0.6821	0.4565
0.1639	0.00717	0.3686	0.06528	0.7618	0.6708
0.1643	0.00709	0.3796	0.07241	0.8450	0.9553
0.1679	0.00756	0.3229	0.04558	0.8915	1.155
0.1689	0.00782	0.3245	0.04562	0.9750	1.560
0.1841	0.00933	0.3402	0.05271	0.9501	1.453
0.1928	0.01065	0.3635	0.06396	1.0221	1.838
0.1965	0.01129	0.3792	0.07187		
1.206	3.221	1.919	14.11	2.945	50.28
1.222	3.419	2.044	17.21	3.049	56.12
1.274	3.863	2.092	18.23	3.191	64.11
1.381	5.084	2.230	22.27	3.296	70.38
1.444	5.905	2.297	24.07	3.565	78.57
1.503	6.669	2.407	27.89	3.710	88.12
1.572	7.751	2.506	31.12	3.862	100.3
1.630	8.594	2.591	34.09	3.985	109.4
1.767	11.03	2.715	39.48	4.158	125.5
1.866	13.09	2.811	44.08		

<sup>11</sup> American Smelting and Refining Company, South Plainfield, New Jersey.

<sup>10</sup> N. E. Phillips, Phys. Rev. 134, A385 (1964).

TABLE II. The heat capacity of indium:  $H = 1000$  Oe. The units of heat capacity are  $\text{mJ mole}^{-1} \text{deg}^{-1}$ .

$T$	$C$	$T$	$C$	$T$	$C$
0.08560	0.2762	0.1425	0.2982	0.3298	0.6198
0.08659	0.2745	0.1570	0.3181	0.3304	0.6210
0.08774	0.2753	0.1658	0.3273	0.3535	0.6697
0.08897	0.2761	0.1705	0.3328	0.3620	0.6884
0.09231	0.2755	0.1725	0.3357	0.3652	0.6950
0.09532	0.2804	0.1824	0.3504	0.3997	0.7728
0.09575	0.2759	0.1904	0.3627	0.4011	0.7765
0.09884	0.2755	0.1906	0.3635	0.4357	0.8581
0.09995	0.2732	0.2008	0.3794	0.4396	0.8684
0.1055	0.2809	0.2118	0.3972	0.4726	0.9533
0.1055	0.2734	0.2210	0.4141	0.4773	0.9656
0.1095	0.2744	0.2362	0.4395	0.5239	1.092
0.1166	0.2772	0.2439	0.4522	0.5763	1.248
0.1170	0.2775	0.2630	0.4882	0.6563	1.519
0.1214	0.2802	0.2703	0.5024	0.7955	2.073
0.1288	0.2859	0.2908	0.5396	0.7216	1.764
0.1296	0.2865	0.2990	0.5578	0.8721	2.427
0.1344	0.2932	0.3003	0.5597		
0.1422	0.2986	0.3207	0.6015		
1.216	4.656	1.8940	13.40	3.079	50.42
1.244	4.900	1.952	14.50	3.189	56.12
1.297	5.382	2.056	16.54	3.289	61.17
1.351	5.883	2.120	17.91	3.449	70.75
1.409	6.501	2.225	20.41	3.536	76.08
1.474	7.206	2.303	22.33	3.720	87.62
1.533	7.911	2.406	25.15	3.818	96.11
1.608	8.906	2.496	27.85	4.009	111.0
1.661	9.668	2.599	31.03	4.145	123.9
1.746	10.88	2.842	40.04		
1.800	11.76	2.935	44.04		

deg and a preliminary value of  $\gamma$ . The final value of  $\gamma$  was determined by inspection of a series of plots of  $C_{ln}/T^3 = (C_n - 1.01 \times 10^{-3} T^{-2} - \gamma T)/T^3$  for different values of  $\gamma$  (see Fig. 5). In view of the large experimental error in  $C_{ln}$  below about  $0.5^\circ\text{K}$ , points in that region were given relatively little weight and the plot for  $\gamma = 1.69 \text{ mJ mole}^{-1} \text{deg}^{-2}$  was chosen as giving the most reasonable temperature dependence of  $C_{ln}$ . With this value of  $\gamma$ , the first two terms of Eq. (4) are a good approximation for  $T \leq 2^\circ\text{K}$  and the values of  $\alpha_n$  and  $\beta_n$  are  $1.42 \text{ mJ mole}^{-1} \text{deg}^{-4}$  and  $0.023 \text{ mJ mole}^{-1} \text{deg}^{-6}$ , respectively. In Figs. 6 and 7,  $(C_n - C_h)/T$  is plotted versus  $T^2$  and compared with the straight line representing the values of  $\gamma$  and  $\alpha_n$ . The experimental points

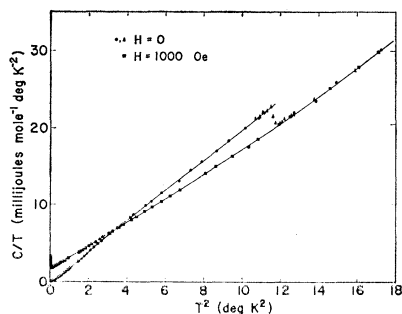


FIG. 3. The normal and superconducting-state heat capacities of indium:  $0.1$  to  $4.2^\circ\text{K}$ .  $\blacktriangle$ : points taken with small temperature increments.

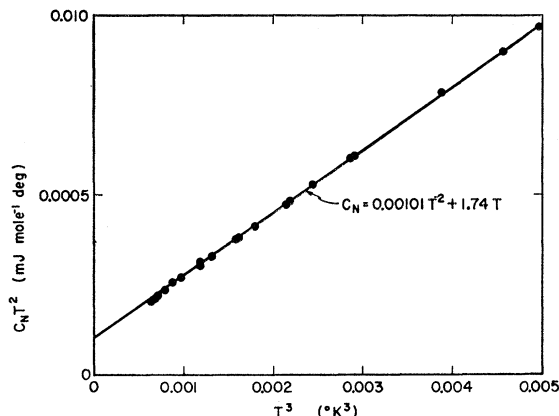


FIG. 4. Graph used to determine the hyperfine contribution to the normal-state heat capacity of indium.

near  $0.15^\circ\text{K}$  are about  $2\%$  higher than the line but this discrepancy is not necessarily significant, since the experimental accuracy is only about  $1\%$  and  $C_h$  is an appreciable part of  $C_n$  at this temperature. The same discrepancy appears in Fig. 4, as a slope greater than that corresponding to  $\gamma = 1.69 \text{ mJ mole}^{-1} \text{deg}^{-2}$ .

### C. Analysis of Superconducting-State Data

Figures 6 and 7 also show the superconducting-state points. The absence of the  $T^{-2}$  term in the superconducting state has also been observed in gallium<sup>10</sup> and mercury,<sup>12</sup> and is a consequence of the long spin-lattice relaxation time  $T_1$ . Neither  $T_1$  nor the Knight shift has been measured in solid indium, but the discussion by Knight, Berger, and Heine<sup>13</sup> suggests that, at the melting point, they are about the same as in the liquid. This assumption makes it possible to estimate  $T_1 T = 0.8 \text{ deg sec}$  from the Knight shift data for liquid indium<sup>13</sup> and the Korringa relation.<sup>14</sup> This prediction is reasonably consistent with the  $5 \text{ sec}$  time constant of the temperature-measuring apparatus and the failure to detect any unusual time effects in the normal-state measurements. The increase in  $T_1$  that is expected to accompany the transition to the superconducting state<sup>15,16</sup> easily accounts for the absence of the hyperfine term there.

At temperatures below  $0.35^\circ\text{K}$ , the measured heat capacity in the superconducting state is  $0.011T + 1.22T^3 \text{ mJ mole}^{-1} \text{deg}^{-1}$ . The term proportional to  $T$  was unexpected, but a similar term was found in tin and also in lead and mercury.<sup>12</sup> It is apparently associated with a small amount ( $0.6\%$  for the indium sample) of "frozen in" normal-state material, which is produced by the exposure of the sample to the stray field of the magnet

<sup>12</sup> N. E. Phillips, M. H. Lambert, and W. R. Gardner, *Rev. Mod. Phys.* **36**, 131 (1964).

<sup>13</sup> W. D. Knight, A. G. Berger, and V. Heine, *Ann. Phys.* **8**, 173 (1959).

<sup>14</sup> J. Korringa, *Physica* **16**, 601 (1954).

<sup>15</sup> L. C. Hebel and C. P. Slichter, *Phys. Rev.* **113**, 1504 (1959).

<sup>16</sup> L. C. Hebel, *Phys. Rev.* **116**, 79 (1959).

used to magnetize the cooling salt. This interpretation of the linear term in the heat capacity of mercury has been tested<sup>12</sup> by making very precise heat-capacity measurements just above 1°K. For a sample cooled in zero field, the application and subsequent removal of a field greater than critical produced an increase in heat capacity approximately equal to the linear term. We therefore conclude that for  $T \leq 0.35^\circ\text{K}$ ,  $C_s = 1.22T^3$  mJ mole<sup>-1</sup> deg<sup>-1</sup>.

#### D. Comparison with Other Experiments

In Table III, some of the parameters characterizing the heat capacity of the two states are compared with other experimental data.

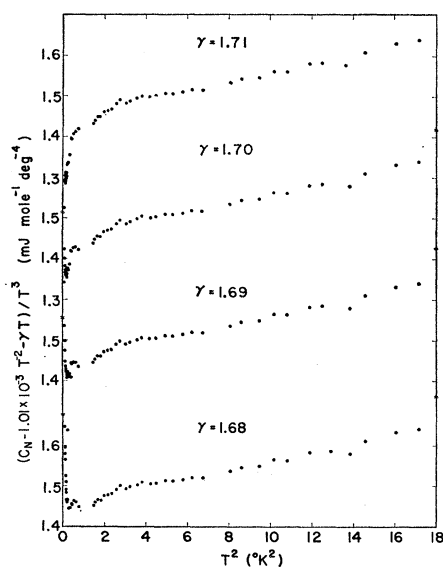


FIG. 5. The normal-state lattice heat capacity of indium corresponding to several different  $\gamma$  values.

A comparison with the normal-state measurements by Bryant and Keesom in the region below 2°K can be made conveniently on the basis of the values of  $\gamma$ ,  $\alpha_n$ , and  $\beta_n$ . Of particular interest is the fact that our value of  $\alpha_n$  is 7% lower than the average for their two samples and 9% lower than their preliminary estimate. Part of this discrepancy is produced by systematic differences in the experimental data; our points are in good agreement with theirs near 1°K, about 1% lower at higher temperatures, and an average of 2% higher below 0.8°K (see Fig. 6). Although these differences must be considered reasonable for independent calorimetric measurements at these temperatures, they do have a significant effect on the interpretation of the data. Bryant and Keesom mention an improvement in their temperature measurements that was introduced after their measurements on indium but before their measurements on tin. Since their lowest temperature points for tin are, on the average slightly higher than ours (see Fig. 10) rather

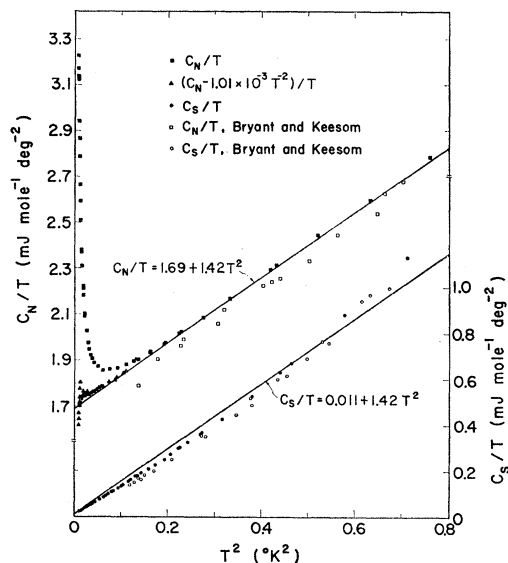


FIG. 6. The normal and superconducting-state heat capacities of indium: 0.1 to 0.9°K.

than 2% low as for indium, this may show that the temperature scale they used for their indium measurements led to low values of the heat capacity in the region below 0.8°K. In addition, Fig. 7 of their paper suggests that they assigned a lower  $\gamma$  value and a higher  $\alpha_n$  value in order to represent  $C_{ln}$  by the first two terms of Eq. (4) over a wider temperature range.

In the superconducting state our low-temperature points are consistently higher than those of Bryant and Keesom, but a large part of the difference is accounted for by the linear term in our data; after subtraction of this term our data are again about 2% higher than their lowest points. Bryant and Keesom assumed that their measured points included the nuclear quadrupole heat capacity and subtracted an estimate of this term from

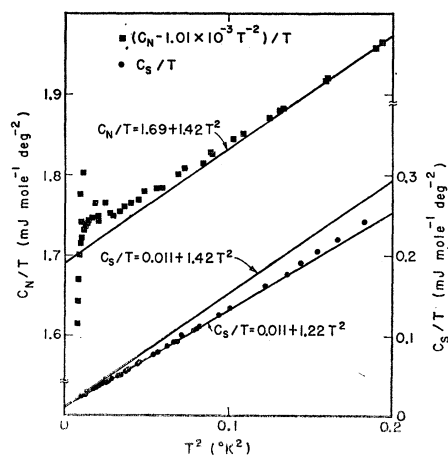


FIG. 7. The normal and superconducting-state heat capacities of indium: 0.1 to 0.45°K.

TABLE III. Summary of calorimetric and related experimental data for indium.

Measurement	$T$ (°K)	$\gamma$ (mJ mole <sup>-1</sup> deg <sup>-2</sup> )	$\alpha_n$ (mJ mole <sup>-1</sup> deg <sup>-4</sup> )	$\alpha_s$ (mJ mole <sup>-1</sup> deg <sup>-4</sup> )	$T_c$ (°K)	$H_0$ (Oe)
Heat capacity						
This work	0.1 - 4.2	1.69	1.42	1.22	3.405	285
Bryant and Keesom <sup>a</sup>	0.35- 4.2	1.61, 1.59	1.50, 1.53		3.403	284
Clement and Quinnell <sup>b</sup>	1.7 -21	1.81	1.50		3.387	
Elastic constants						
Chandrasekhar and Rayne <sup>c</sup>	1.4		1.41	1.41		
Critical field						
Shaw, Mapother and Hopkins <sup>d</sup>	1 - 3.4				3.408	285.7
Finnemore and Mapother <sup>e</sup>	0.3 - 3.4	1.66			3.407	282.66

<sup>a</sup> See Ref. 2.

<sup>b</sup> See Ref. 17.

<sup>c</sup> See Ref. 4.

<sup>d</sup> R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

<sup>e</sup> See Ref. 18.

$C_s$  to give an upper limit of 1.1 mJ mole<sup>-1</sup> deg<sup>-4</sup> for  $C_{ln}/T^3$  at 0.35°K. The work presented here shows that this term is not included and their data therefore correspond to  $C_{ln}/T^3 \leq 1.2$  mJ mole<sup>-1</sup> deg<sup>-4</sup>, in good agreement with the value reported here.

To summarize the comparison of our data with those of Bryant and Keesom, the agreement in the actual measured heat capacities is as good as can be expected but differences in the analyses of the data lead to different estimates of the discrepancy between  $C_{ln}$  and  $C_{ln}$ . Bryant and Keesom found  $C_{ln}/C_{ln} = 1.4$  at 0.35°K and we find the smaller but still significant discrepancy  $C_{ln}/C_{ln} = 1.16$ , at temperatures between 0.1 and 0.35°K.

The heat capacity data reported here are also in reasonable agreement with the values reported by Clement and Quinnell<sup>17</sup> above 1.7°K. The apparent difference in Table III is again largely a matter of the way the data are analyzed.

Chandrasekhar and Rayne<sup>4</sup> have measured the elastic

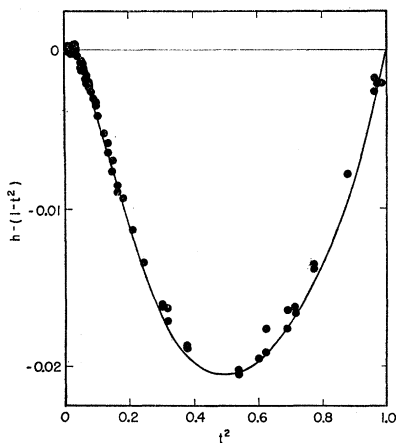


FIG. 8. Deviation of the critical field of indium from a parabola. The curve is calculated from smoothed heat capacity data. ●: critical field measurements by Finnemore and Mapother.

<sup>17</sup> J. R. Clement and E. H. Quinnell, Phys. Rev. **92**, 258 (1953).

constants of indium at 1.4°K, and find the same value in both the normal and superconducting states, within 1 part in 10<sup>4</sup>. The actual values correspond to  $\alpha_s = \alpha_n = 1.41 \pm 0.04$  mJ mole<sup>-1</sup> deg<sup>-4</sup>, in excellent agreement with our value of  $\alpha_n$  and in obvious disagreement with our value of  $\alpha_s$ . The experimental error in the calorimetric  $\alpha_n$  is difficult to estimate but it is likely to be 2% or less, as long as the  $T^3$  region of  $C_{ln}$  is not much shorter than has been assumed in the analysis.

The critical magnetic field  $H_c$  was obtained by carrying out the necessary integrations on smoothed values of  $C_n - C_s$ . The linear term in the measured heat capacity in the superconducting state was subtracted and  $C_n$  and  $C_s$  were extrapolated to  $T=0$  as  $1.69T + 1.42T^3$  and  $1.22T^3$  mJ/mole deg, respectively. The transition temperature  $T_c$  was taken as the temperature at which the entropies of the two states were equal. The value obtained in this way, 3.405°K, was consistent with heat capacity points and warming curves taken through the zero-field transition. The critical field at  $T=0$ ,  $H_0$ , was found to be 285 Oe. The temperature dependence of  $H_c$  is given graphically in Figs. 8 and 9 as the deviation from a parabola,  $D(t) = h - (1-t^2)$ , in which  $h = H_c/H_0$  and  $t = T/T_c$ .

The most accurate value of  $H_0$  available is probably that reported by Finnemore and Mapother,<sup>18</sup>  $H_0 = 282.66$  Oe. For their lowest-temperature measurements, near 0.3°K,  $H_c$  is within 1% of  $H_0$  and it seems unlikely that the extrapolation in  $T=0$  could introduce an error as large as the difference between their result and ours. A large part of this difference is probably a consequence of the magnification of systematic errors in calculating  $C_n - C_s$ , which is small relative to  $C_n$  and  $C_s$  above 1°K.  $D(t)$  can be expected to be less sensitive to systematic errors in  $C_n - C_s$  than  $H_0$ , and therefore the excellent agreement between our values of  $D(t)$  and those of Finnemore and Mapother (also shown in Figs.

<sup>18</sup> D. K. Finnemore and D. E. Mapother, Technical Report No. 2, OOR Project No. 2771-P (unpublished), and private communication.

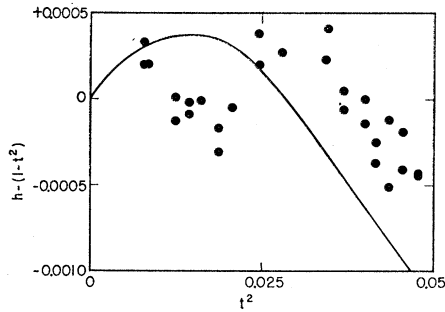


FIG. 9. Detail from Fig. 8, showing the data at temperatures below  $0.7^\circ\text{K}$ .

8 and 9) is not surprising in spite of the discrepancy in  $H_0$ . The positive values of  $D(l)$  obtained from the heat capacity points at  $l^2 < 0.025$  are a direct consequence of the inequality  $\alpha_n > \alpha_s$ .  $H_c$  is very insensitive to the properties of the superconducting state at these temperatures and, as shown in Fig. 9, this feature would not be apparent in  $H_c$  measurements, even with the high precision obtained by Finnemore and Mapother. The agreement between the  $\gamma$  value reported here and that calculated from the critical field data is satisfactory. The two values are comparably sensitive to temperature scale errors and these, rather than scatter in the experimental points, probably limit the accuracy.

Indium nuclei have spin  $I = \frac{9}{2}$ . In the metal, the ten degenerate states of a free nucleus are split into five doublets by the interaction between the nuclear electric-quadrupole moment and an electric-field gradient. The nuclear magnetic dipole moments are large enough that the splitting of the doublets by the 1000-Oe magnetic field used to quench superconductivity cannot be neglected. The coefficient  $A$  in Eq. (6), calculated from the quadrupole coupling constants<sup>19,20</sup> and magnetic moments,<sup>21</sup> is  $A = (0.90 + 0.14 \cos^2\phi) \times 10^{-3}$  mJ mole<sup>-1</sup> deg, where  $\phi$  is the angle between the applied magnetic field and the  $c$  axis of the crystal. The observed  $A$  falls within the range of possible values but we have been unable to measure  $\phi$  and make an exact comparison. It appears that handling the sample has brought about a recrystallization of the surface and made it impossible to obtain clear x-ray patterns.

#### IV. HEAT CAPACITY OF TIN

The measurements were made on an 843-g polycrystalline sample that was cast under vacuum from 99.9999% tin supplied by Cominco Products Inc.<sup>22</sup> The experimental points are given in Tables IV and V and plotted as  $C/T$  versus  $T^2$  in Figs. 10 and 11.

<sup>19</sup> R. R. Hewitt and W. D. Knight, Phys. Rev. Letters **3**, 18 (1959).

<sup>20</sup> W. W. Simmons and C. P. Slichter, Phys. Rev. **121**, 1580 (1961).

<sup>21</sup> D. Strominger, J. M. Hollander, and G. T. Seaborg, Rev. Mod. Phys. **30**, 585 (1958).

<sup>22</sup> Cominco Products Inc., Spokane, Washington.

TABLE IV. The heat capacity of tin:  $H=0$ . The units of heat capacity are mJ mole<sup>-1</sup> deg<sup>-1</sup>.

$T$	$C$	$T$	$C$	$T$	$C$
0.1456	0.001585	0.3382	0.01056	0.3082	0.008556
0.1519	0.001461	0.3402	0.01118	0.3242	0.009727
0.1569	0.001566	0.3537	0.01218	0.3287	0.01009
0.1667	0.001870	0.3635	0.01332	0.3367	0.01075
0.1676	0.001902	0.3577	0.01282	0.3543	0.01231
0.1720	0.001921	0.3672	0.01359	0.3636	0.01329
0.2305	0.003998	0.3703	0.01392	0.3736	0.01433
0.2380	0.004477	0.1558	0.001647	0.3881	0.01590
0.2384	0.004429	0.1601	0.001673	0.3900	0.01620
0.2523	0.004629	0.1616	0.001800	0.4058	0.01807
0.2539	0.004953	0.1725	0.002074	0.4112	0.01892
0.2540	0.005036	0.1770	0.002139	0.4419	0.02327
0.2572	0.005063	0.2009	0.002925	0.4434	0.02339
0.2575	0.005052	0.2014	0.002892	0.4554	0.02552
0.2818	0.006604	0.2174	0.003514	0.4837	0.03032
0.2875	0.006939	0.2279	0.003913	0.5150	0.03698
0.2884	0.007198	0.2288	0.004013	0.5383	0.04298
0.2894	0.007019	0.2333	0.004129	0.5749	0.05460
0.2914	0.007282	0.2338	0.004060	0.5826	0.05661
0.2981	0.007626	0.2340	0.004179	0.6170	0.07003
0.3024	0.007996	0.2345	0.004058	0.6557	0.07992
0.3067	0.008135	0.2525	0.004968	0.7016	0.1150
0.3128	0.008928	0.2564	0.005300	0.7879	0.1887
0.3178	0.009192	0.2667	0.005724	0.8596	0.2714
0.3195	0.009500	0.2831	0.006727	0.9203	0.3642
0.3200	0.009459	0.2840	0.006765	0.9564	0.4271
0.3333	0.01029	0.3021	0.008097	1.061	0.6489

The superconducting-state heat capacity includes a linear term which we again associate with the presence of a small amount of "frozen-in" normal material. After subtraction of the linear term of the superconducting state, points below about  $0.45^\circ\text{K}$  are represented by  $C_s = 0.246T^3$  mJ mole<sup>-1</sup> deg<sup>-1</sup> and we therefore conclude that  $\alpha_s = 0.246$  mJ mole<sup>-1</sup> deg<sup>-4</sup>.

No  $T^{-2}$  term is expected in  $C_n$ , even in the 1000-Oe field used to suppress superconductivity, because the naturally occurring tin isotopes have zero electric quadrupole moment and only small magnetic dipole mo-

TABLE V. The heat capacity of tin:  $H=1000$  Oe. The units of heat capacity are mJ mole<sup>-1</sup> deg<sup>-1</sup>.

$T$	$C$	$T$	$C$	$T$	$C$
0.09269	0.1615	0.1780	0.3141	0.3973	0.7153
0.09474	0.1645	0.1821	0.3204	0.4339	0.7928
0.09517	0.1658	0.1865	0.3297	0.4408	0.7998
0.10373	0.1754	0.1966	0.3493	0.4886	0.8998
0.10470	0.1756	0.2003	0.3529	0.5137	0.9439
0.11136	0.1887	0.2051	0.3646	0.5264	0.9734
0.11165	0.1887	0.2182	0.3888	0.5423	1.003
0.11734	0.2043	0.2204	0.3913	0.5681	1.057
0.11868	0.2085	0.2301	0.4088	0.6260	1.180
0.1217	0.2162	0.2402	0.4266	0.6374	1.204
0.1286	0.2318	0.2438	0.4313	0.6923	1.319
0.1315	0.2369	0.2594	0.4616	0.6932	1.325
0.1342	0.2367	0.2652	0.4737	0.7637	1.473
0.1410	0.2488	0.2888	0.5148	0.8199	1.597
0.1453	0.2555	0.2925	0.5209	0.8393	1.643
0.1480	0.2597	0.2978	0.5301	0.8941	1.774
0.1485	0.2602	0.3198	0.5727	0.9341	1.862
0.1603	0.2797	0.3592	0.6647	0.9637	1.944
0.1625	0.2847	0.3550	0.6362	1.032	2.107
0.1652	0.2900	0.3948	0.7158	1.037	2.110
				1.126	2.338

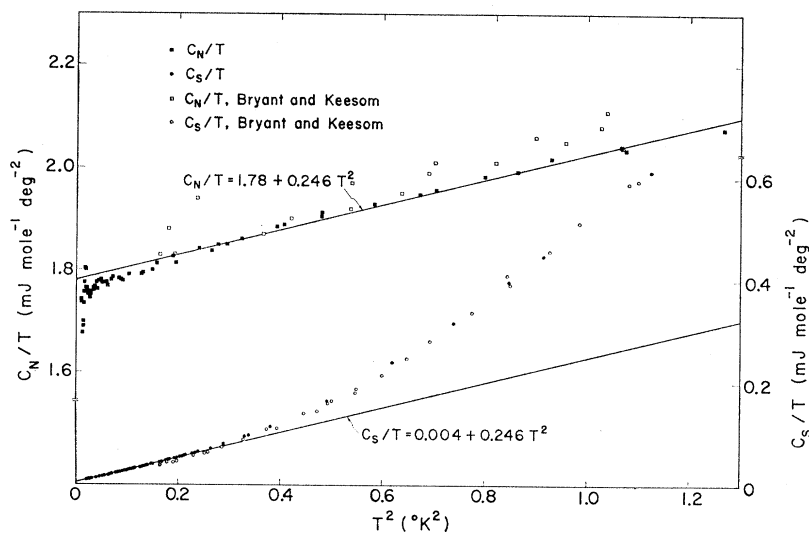


FIG. 10. The normal and superconducting-state heat capacities of tin: 0.1 to 1.1°K.

ments. An accurate calorimetric evaluation of  $\alpha_n$  is more difficult than for indium because, as shown by the measurements by Bryant and Keesom,<sup>2</sup> the effects of dispersion on  $C_{ln}$  become important at temperatures where  $C_{ln}$  is smaller relative to  $\gamma T$ . For example, at 2°K the  $T^5$  term is about 6% of  $C_{ln}$ , and  $C_{ln}$  is still only about 35% of  $C_n$ . For our highest temperature points  $C_{ln}$  is only 13% of  $C_n$ , so the uncertainty in  $\alpha_n$  is considerable; but within the expected accuracy, the normal-state data are represented by  $\alpha_n = \alpha_s$  and  $\gamma = 1.78 \text{ mJ mole}^{-1} \text{ deg}^{-2}$ .

The parameters  $\gamma$ ,  $\alpha_n$ , and  $\alpha_s$  are compared with other experimental data in Table VI. Our  $\alpha_n$  is in good agreement with that obtained by Bryant and Keesom from experimental data extending to higher temperatures and an analysis based on the first two terms of Eq. (4).<sup>2</sup> They also conclude that their lowest superconducting state points are consistent with  $\alpha_s = \alpha_n$ . Except for the  $\alpha_n$  reported by Corak and Satterthwaite,<sup>23</sup> the calorimetric values of  $\alpha_s$  and  $\alpha_n$  agree with the  $\alpha_n$  calculated from

the elastic constants<sup>24</sup> to within the quoted experimental error in that measurement alone. Corak and Satterthwaite obtained a higher value of  $\alpha_n$  from calorimetric data above 1.2°K, but analysis of their data using two or more terms of Eq. (4) has shown<sup>24,25</sup> that they give lower values than the one originally reported. All available experimental data are therefore consistent with the equality  $\alpha_n = \alpha_s$  and a value in the vicinity of  $0.238$  to  $0.246 \text{ mJ mole}^{-1} \text{ deg}^{-4}$ .

Although the  $\gamma$  value reported by Bryant and Keesom is in reasonable agreement with ours, it is slightly higher, whereas for indium their value was lower. The same trend is shown by the individual heat-capacity points (compare Figs. 5 and 10) and, as mentioned in in Sec. IIIB, may be a consequence of the change in their temperature scale that was introduced between their indium and tin measurements. The discrepancy between our  $\gamma$  and that calculated by Finnemore and Mapother<sup>18</sup> from critical-field data is similar to the corresponding discrepancy for indium discussed in Sec. IIIB.

## V. DISCUSSION

### A. Interpretation of Experimental Results

The foregoing analysis of our data, and the earlier heat-capacity measurements on indium by Bryant and Keesom, suggest that at least one of the assumptions expressed by Eqs. (1), (2), and (3) is not valid. In the following discussion the only generalization of these equations that will be considered is that  $C_{ln}$  and  $C_{ln}$  may be different. For the comparison of the experiments with existing theories it is unnecessary to consider the possibility that the heat capacity is not the sum of

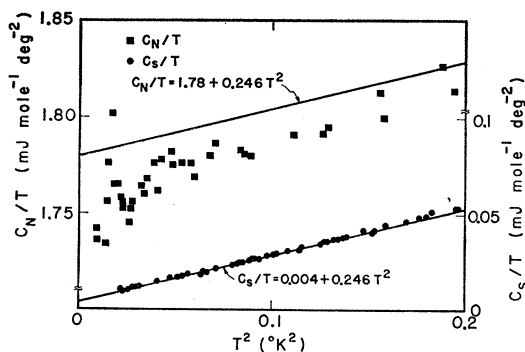


FIG. 11. The normal and superconducting-state heat capacities of tin: 0.1 to 0.45°K.

<sup>23</sup> W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1959).

<sup>24</sup> J. A. Rayne and B. S. Chandrasekhar, Phys. Rev. **120**, 1658 (1960).

<sup>25</sup> T. H. K. Barron and J. A. Morrison, Can. J. Phys. **35**, 799 (1957).



TABLE VI. Summary of calorimetric and related experimental data for tin.

Measurement	$T$ (°K)	$\gamma$ (mJ mole <sup>-1</sup> deg <sup>-2</sup> )	$\alpha_n$ (mJ mole <sup>-1</sup> deg <sup>-4</sup> )	$\alpha_s$ (mJ mole <sup>-1</sup> deg <sup>-4</sup> )	$T_c$ (°K)	$H_0$ (Oe)
Heat capacity						
This work	0.1 -1.0	1.78	(0.246)	0.246		
Bryant and Keesom <sup>a</sup>	0.4 -4.2	1.80		0.242	3.701	306
Corak and Satterthwaite <sup>b</sup>	1.2 -4.5	1.75		0.262	3.722	303
Zavaritskii <sup>c</sup>	0.15-4			0.236		
Elastic constants						
Rayne and Chandrasekhar <sup>d</sup>	4.2		0.238			
Critical field						
Shaw, Mapother and Hopkins <sup>e</sup>	1 -3.7				3.722	308.7
Finnemore and Mapother <sup>f</sup>	0.3 -3.7	1.74			3.722	305.5

<sup>a</sup> See Ref. 2.<sup>b</sup> See Ref. 23.<sup>c</sup> N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. 33, 1085 (1957) [English transl.: Soviet Phys.—JETP 6, 837 (1957)].<sup>d</sup> See Ref. 24.<sup>e</sup> R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. 120, 88 (1960).<sup>f</sup> See Ref. 18.

separable lattice and electronic terms, as long as  $C_{ls}$  and  $C_{ln}$  are understood in a more general way than has been usual.

For tin, at temperatures below 0.45°K,  $C_s$  is proportional to  $T^3$  and the identification of this  $T^3$  term with  $C_{ls}$  permits an evaluation of  $\alpha_s$ . The magnitude and temperature dependence of  $C_{ln}$  make the calorimetric determination of  $\alpha_n$  less accurate, but there is no evidence for a discrepancy between  $\alpha_s$  and  $\alpha_n$ . Because of the uncertainty in the calorimetric  $\alpha_n$ , the agreement between the elastic constants and the calorimetric  $\alpha_s$  is important in establishing the equality  $\alpha_s = \alpha_n$ . Figure 12 shows that  $C_{es}$ , defined by  $C_{es} = C_s - \alpha_s T^3$ , has the expected exponential temperature dependence; for  $3 < T_c/T < 9$ ,  $C_{es} = 7.85\gamma T_c \exp(-1.42T_c/T)$ . Since the BCS

theory gives a  $C_{es}$  proportional to  $\exp(-1.44T_c/T)$  in this temperature region and an energy gap at  $T=0$  of  $3.50kT_c$ , the observed  $C_{es}$  corresponds to a 0°K energy gap of approximately  $3.45kT_c$ . The possibility that the energy gap is anisotropic complicates the comparison of values obtained by different methods but, as shown in Table VII, the calorimetric value is in good agreement

TABLE VII. Energy gap at 0°K in units  $kT_c$ .

Measurement	Tin	Indium
This work	3.45	3.26-3.77
Infrared absorption in the bulk metal <sup>a</sup>	3.6	4.1
Infrared absorption in films <sup>b</sup>	3.3	3.9
Electron tunneling <sup>c</sup>	3.5	3.6

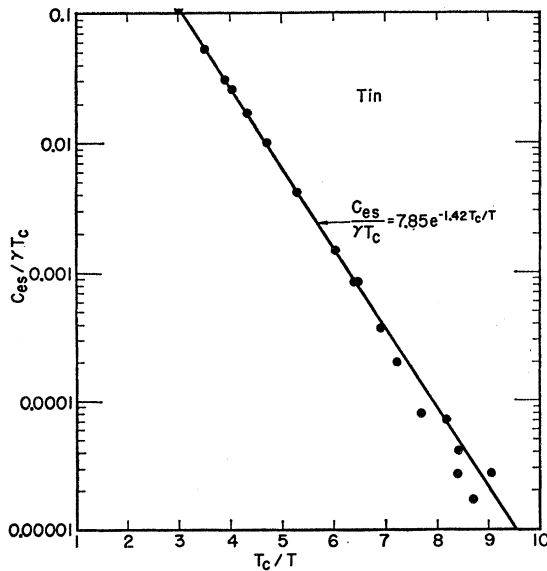
<sup>a</sup> P. L. Richards and M. Tinkham, Phys. Rev. 119, 575 (1960).<sup>b</sup> D. M. Ginsberg and M. Tinkham, Phys. Rev. 118, 990 (1960).<sup>c</sup> I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961).

FIG. 12. The superconducting-state electronic heat capacity of tin.

with those obtained by several other measurements that are sensitive to the size of the gap at  $T \ll T_c$ . The behavior of tin is thus entirely consistent with Eqs. (1), (2), and (3) and the expected temperature dependence of  $C_{es}$ ; any discrepancy between  $C_{ls}$  and  $C_{ln}$  is less than the experimental error.

For indium, the analysis of the normal-state data in Sec. IIIB follows a conventional procedure and we would ordinarily assume that the resulting  $\alpha_n$  value was correct within about 2%. However, if this value is correct, the total superconducting-state heat capacity is less than the normal-state lattice heat capacity at temperatures below 0.65°K and, consequently,  $C_{ls} < C_{ln}$ . Since this difference between  $C_{ls}$  and  $C_{ln}$  is difficult to account for theoretically (see below), and since it is evidently not a general feature of the superconducting transition, it is interesting to consider in detail the possibility that  $\alpha_n$  was overestimated and that the indium data could be represented by the same lattice heat capacity in both normal and superconducting states.

This is possible even though the analysis in Sec. III gave a significant discrepancy between  $\alpha_n$  and  $\alpha_s$ , because the values of these parameters were chosen to fit the experimental data in different temperature intervals;  $\alpha_s$  was determined by the measurements at temperatures for which  $C_{es} \ll \alpha_s T^3$ , i.e., at  $T \leq 0.35^\circ\text{K}$ , but  $\alpha_n T^3$  is a small part of  $C_n$  in that temperature range and the value of  $\alpha_n$  was largely determined by the measurements at  $T \geq 0.4^\circ\text{K}$ . More accurate measurements at lower temperatures have generally tended to give lower calorimetric  $\alpha_n$ 's and there are metals (e.g., gallium<sup>10,26</sup> and cadmium<sup>10,27</sup>) for which deviations from the  $T^3$  lattice heat capacity amount to several percent at  $T \approx \theta_0/200$ , which corresponds to  $0.5^\circ\text{K}$  for indium. The possibility that  $\alpha_n$  was overestimated and that more accurate measurements of  $C_n$  at  $T < 0.4^\circ\text{K}$  would reveal a limiting slope of  $(C_n - C_h)/T$  versus  $T^2$  equal to that of  $C_s/T$  versus  $T^2$  should therefore be considered. This possibility is actually suggested by the deviation of the lowest temperature  $C_n - C_h$  points from the straight line of Figs. 6 and 7. An obvious feature of these figures is the possibility of representing the  $(C_n - C_h)/T$  and  $C_s/T$  points at  $T^2 \lesssim 0.3^\circ\text{K}^2$  by parallel curves, which would correspond to equal lattice heat capacities. It was pointed out in Sec. IIIB that these deviations are within the probable experimental error and therefore not necessarily significant but, for the same reason, the possibility of a change in slope of  $(C_n - C_h)/T$  versus  $T^2$  near  $T^2 \approx 0.15^\circ\text{K}^2$  would have to be considered even if the experimental points did fall on the line.

The effect of such an interpretation of the data on the apparent temperature dependence of the lattice heat capacity is shown in Fig. 13 as a plot of the effective Debye temperature  $\theta$ , defined by equating the lattice heat capacity to  $(12/5)\pi^4 R (T/\theta)^3$ , against  $T$ . The open circles represent the  $C_{ln}$  values obtained in Sec. IIIB and the solid curve represents the extrapolation to  $T = 0$  equivalent to the straight line of Figs. 6 and 7. The dashed curve shows a lattice heat capacity that could be assigned to both normal and superconducting states, within the experimental error. It corresponds to a curve for  $(C_n - C_h)/T$  versus  $T^2$  that follows the individual heat capacity points above  $T^2 \approx 0.7^\circ\text{K}^2$  and the straight line of Figs. 6 and 7 for  $0.15 < T^2 < 0.7^\circ\text{K}^2$ , but goes over smoothly to the line  $(C_n - C_h)/T = 1.72 + 1.22T^2$  mJ mole<sup>-1</sup> deg<sup>-2</sup> below  $T^2 \approx 0.15^\circ\text{K}^2$ . It differs from the original line by no more than the possible experimental error, but is actually a better representation of the low-temperature points, and corresponds to an  $\alpha_n$  that is equal to  $\alpha_s$ . This interpretation of the data would require an unusual frequency spectrum (the higher temperature measurements by Clement and Quinnell<sup>17</sup> confirm the negative curvature of the  $\theta$  plot near  $4^\circ\text{K}$ ), but this seems to be insufficient reason for excluding it

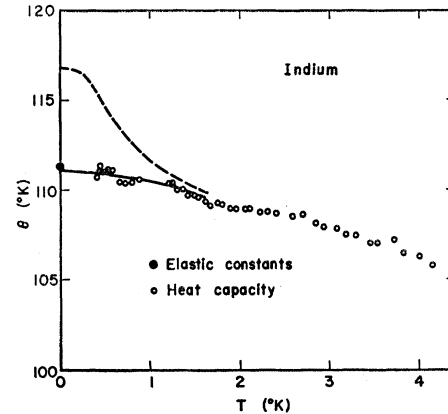


FIG. 13. The effective Debye temperature of indium.  $\circ$ : normal-state lattice heat capacity obtained in Sec. IIIB. The solid curve is equivalent to the straight line of Figs. 6 and 7. The dashed curve is a possible superconducting-state lattice heat capacity.

as impossible, particularly for a metal that is as anisotropic acoustically as indium.

Comparison of the normal-state heat capacity with the elastic constants provides a more obvious reason for accepting the  $\alpha_n$  value derived in Sec. IIIB and, consequently, the discrepancy between  $C_{ln}$  and  $C_{ls}$ . Excluding metals for which an accurate calorimetric determination of  $\alpha_n$  is difficult, most of the available data support the assumption that the  $\alpha_n$  calculated from elastic constants is the same as the calorimetric  $\alpha_n$ . The discrepancies that have been reported<sup>28</sup> have usually been for metals for which the  $T^5$  term could be important at temperatures so low that  $C_{ln}$  is still only a small part of  $C_n$ , and in some of these cases heat capacity measurements below  $1^\circ\text{K}$  have resolved the discrepancy.<sup>10,27,29</sup> For indium, the only  $\theta - T$  curve that could represent the lattice heat capacities of both normal and superconducting states and also agree with the elastic constants is one that follows the points in Fig. 13 above  $1.5^\circ\text{K}$  and the dashed curve from  $1.5^\circ\text{K}$  to  $0.1^\circ\text{K}$ , but then drops to  $\theta_0 = 111^\circ\text{K}$  somewhere between  $0.1^\circ\text{K}$  and the temperature corresponding to the frequency of the elastic constants measurements,  $5 \times 10^{-4}^\circ\text{K}$ . Since experimental data on other metals in the normal state offer no precedent for such a  $\theta - T$  curve,<sup>30,31</sup> it seems

<sup>28</sup> The situation was reviewed several years ago by G. A. Alers and J. R. Neighbours, *Rev. Mod. Phys.* **31**, 675 (1959).

<sup>29</sup> C. W. Garland and J. Silverman, *J. Chem. Phys.* **34**, 781 (1961).

<sup>30</sup> It has been reported (D. L. Martin, private communication) that gold has a  $\theta - T$  curve that shows an increase in  $\theta$ , followed by a maximum, as  $T$  increases from  $0^\circ\text{K}$ . However, the maximum occurs at  $T \approx \theta_0/20$ , whereas for indium, the initial rise would have to be complete by  $T < \theta_0/1000$ .

<sup>31</sup> Calculations by L. J. Slutsky and G. Jelinek, *J. Chem. Phys.* **37**, 2727 (1962), for a model employing first- and second-neighbor forces evaluated from the elastic constants, give a negative quartic term in the frequency spectrum of indium and, therefore, a Debye  $\theta$  that increases from  $\theta_0$  as  $T$  increases from  $0^\circ\text{K}$ . However, the coefficient of the quartic term is about  $1/500$  as large as would correspond to this drop in  $\theta$ .

<sup>26</sup> G. Seidel and P. H. Keesom, *Phys. Rev.* **120**, 762 (1960).

<sup>27</sup> D. L. Martin, *Proc. Phys. Soc. (London)* **78**, 1482 (1961).

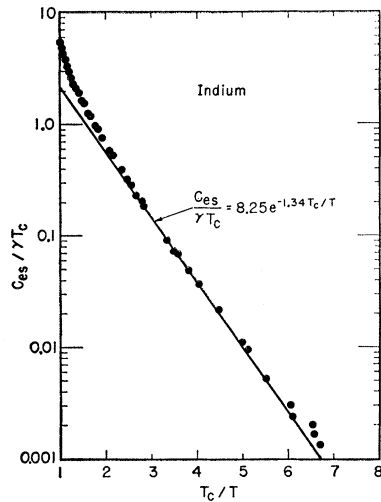


FIG. 14. The superconducting-state electronic heat capacity of indium. The points are based on the assumption that the lattice heat capacity is  $1.22T^3$  mJ mole $^{-1}$  deg $^{-1}$ . Another possibility is discussed in Sec. VA.

more reasonable to accept the inequality of  $C_{ls}$  and  $C_{ln}$ . A difference between  $C_{ls}$  and  $C_{ln}$  of this size certainly does not occur for all superconductors but the existing measurements of  $C_{ls}$  for other superconductors permit no further generalization: for tin  $C_{ls}$ ,  $C_{ln}$ , and the elastic constants all agree; for mercury the elastic constants are not known but  $C_{ls}$  and  $C_{ln}$  agree;<sup>12</sup> for lead<sup>12,32</sup> and for niobium<sup>33,34</sup> there are conflicting experimental results.

The apparent temperature dependence of  $C_{es}$  shows that the dashed curve of Fig. 13 is at least an approximation to  $C_{ls}$ , independently of the interpretation of the normal-state data. As shown in Fig. 14, the assumption that  $C_{ls} = \alpha_s T^3$  gives  $C_{es} = 8.25\gamma T_c \exp(-1.34T_c/T)$  for  $3 < T_c/T < 6$ , corresponding to  $3.26kT_c$  for the energy gap at 0°K. This is clearly an overestimate of  $C_{es}$  near  $T_c$  and comparison with other measurements of the energy gap (see Table VII) suggests that it is also an overestimate in the region 0.5 to 1.5°K. The other measurements are in good agreement with the calorimetric value for tin but conspicuously high in comparison with the  $3.26kT_c$  for indium. It therefore appears that at least part of the difference between  $C_s$  and  $\alpha_s T^3$  in the region just above 0.5°K must be produced by an increase in  $C_{ls}/T^3$  from the low-temperature value  $\alpha_s$ . The assumption that  $C_{ls}$  is represented by the dashed curve of Fig. 13 gives  $C_{es} = 9.40\gamma T_c \exp(-1.55T_c/T)$  at  $2 < T_c/T < 4$  and the more reasonable value  $3.77kT_c$  for the energy gap at 0°K. Below  $T_c/4$ ,  $C_{es}$  decreases with decreasing temperature more rapidly than  $\exp(-1.55T_c/T)$  and drops to zero near 0.6°K, but the discrepancy is less than 2% of  $C_s$  at all temperatures and could be eliminated by a relatively small shift in the dashed curve.

Although the effective Debye temperatures for the

two states can be used as a basis for comparison of the lattice heat capacities, they cannot be taken as a measure of a shift in the frequency spectrum as a whole. If the discrepancy between the normal and superconducting states,  $\Delta\theta_0 = 5.8^\circ\text{K}$ , were produced by a shift of this size in the whole spectrum, it would correspond to a change in the lattice zero-point energy approximately  $10^4$  times as great as the total normal-superconducting energy difference. The actual changes in the frequency spectrum must be such as to leave the average frequency relatively unchanged. As pointed out elsewhere,<sup>12</sup> the Debye-Waller factor, which does depend on the whole frequency spectrum, can be expected to change by an amount corresponding to a much smaller  $\Delta\theta_0$ . Therefore, the failure to detect changes in the Debye-Waller factor at the superconducting transitions in tin<sup>35,36</sup> and indium<sup>37</sup> has no bearing on the reality of the discrepancy in lattice heat capacity and is to be expected, independently of the mechanism producing the discrepancy.

## B. Comparison with Theory

There have been several attempts to provide a theoretical basis for the discrepancy between  $C_{ls}$  and  $C_{ln}$ . In this section the experimental data for indium are compared with the theoretical predictions.

Calculations by Eliashberg<sup>38</sup> suggest that the electron-phonon interaction contributes a  $T^3 \ln T$  term to  $C_n$  but not to  $C_s$ . This term might be included in the  $T^3$  term obtained by analysis of calorimetric data and  $\alpha_n$  would then appear to be larger than  $\alpha_s$ . However, it is  $\alpha_s$  which should agree with the elastic constants, contrary to the experimental result for indium. Furthermore, the calculations are contradicted by the general agreement between calorimetric  $\alpha_n$ 's and elastic constants.

Ferrell<sup>39</sup> has used the difference in response to sound waves of normal and superconducting electrons to derive a modified dispersion relation for phonons in the superconducting state. He finds that phonons with wavelength longer than the coherence distance and energy less than the gap energy are shifted upward in frequency by a constant amount. This produces a negative term proportional to frequency in the frequency spectrum and  $C_{ls}$  becomes the sum of  $\alpha_n T^3$  and a negative  $T^2$  term. As shown in Fig. 15, a relation of this type does not fit the experimental points as well as a single  $T^3$  term. If the decrease in lattice heat capacity that accompanies the transition to the superconducting state is produced by an increase in frequency of the thermally excited vibrational modes, the temperature dependence of  $C_{ls}$  and  $C_{ln}$  shows that the shift

<sup>35</sup> W. K. Wiedemann, P. Kienle, and F. Pobell, *Z. Physik* **166**, 109 (1962).

<sup>36</sup> M. Yaqub and C. Hohenemser, *Phys. Rev.* **127**, 2028 (1962).

<sup>37</sup> P. P. Craig, R. D. Taylor, and D. E. Nagle, *Nuovo Cimento* **22**, 402 (1961).

<sup>38</sup> G. M. Eliashberg, *Zh. Eksperim. i Teor. Fiz.* **43**, 1005 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 780 (1963)].

<sup>39</sup> R. A. Ferrell, *Phys. Rev. Letters* **6**, 541 (1961).

<sup>32</sup> P. H. Keesom and B. J. C. van der Hoeven, *Phys. Letters* **3**, 360 (1963).

<sup>33</sup> A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, *Phys. Rev.* **127**, 1501 (1962).

<sup>34</sup> B. J. C. van der Hoeven and P. H. Keesom, *Bull. Am. Phys. Soc.* **9**, 268 (1964).

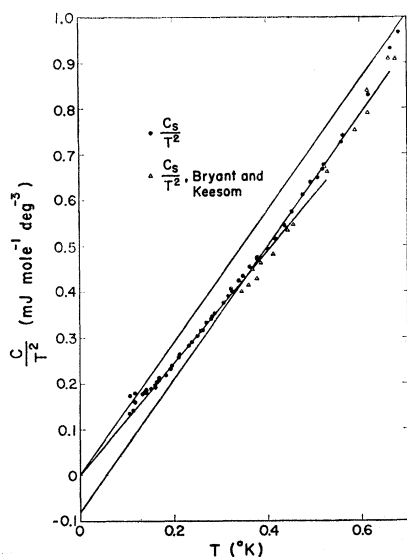


FIG. 15. Comparison of the superconducting-state lattice heat capacity of indium with Ferrell's prediction. The lines through the origin have slopes  $\alpha_n$  and  $\alpha_s$ . The third line also has slope  $\alpha_n$  and represents the temperature dependence predicted by Ferrell.

must be proportional to frequency for the frequencies that determine the heat capacity between 0.1 and 0.35°K. Ferrell's conclusions are also contradicted by calculations by Kulik.<sup>40</sup>

Daunt and Olsen<sup>41</sup> have suggested that the discrepancy between  $C_{Is}$  and  $C_{In}$  is produced by different temperature-dependent zero-point energies in the two states. The temperature dependence of the zero-point energy is suggested by the temperature dependence of the elastic constants and by the relation between the elastic constants and the low-frequency end of the vibration spectrum. Since the high-frequency modes are important in the interaction producing superconductivity, and since the zero-point energy of these modes is so large, it seems possible that changes in their frequency associated with the superconducting transition might make an appreciable contribution to  $C_{Is}$ . It would require only a very small shift in the high-frequency part of the spectrum to produce an energy shift comparable to that indicated by the discrepancy in lattice heat capacities. However, there are several difficulties associated with relating the change in zero-point energy to the elastic constants: (1) The temperature dependence of the elastic constants is not confined to the superconducting state, and the same argument would predict a contribution to the heat capacity of all solids; (2) there would be a latent heat associated with the discontinuity in the bulk modulus at  $T_c$ . It therefore seems

clear that the whole spectrum does not shift in the same way and that any contribution to  $C_{Is}$  from the zero-point energy of the high-frequency modes cannot be calculated from the elastic constants.

## VI. SUMMARY

If the normal-state heat capacity is interpreted in the usual way and, in particular, if it is assumed that the lattice heat capacity is proportional to  $T^3$  for temperatures up to about  $\theta_{0n}/130$ , the calorimetric data for indium show that a decrease in the lattice heat capacity accompanies the transition from the normal to the superconducting state. The validity of this interpretation of the normal-state data is supported by the agreement between the resulting  $\theta_{0n}$  and the value calculated from the elastic constants. The heat-capacity data give  $\theta_{0s}=116.8^\circ\text{K}$  and  $\theta_{0n}=111.0^\circ\text{K}$  whereas the elastic-constants data give  $\theta_{0n}=\theta_{0s}=111.3^\circ\text{K}$ . Any alternative interpretation of the heat-capacity data that gives the same lattice heat capacity in the two states requires an unusual temperature dependence of the lattice heat capacity; and if the calorimetric data are to agree with the elastic constants, the  $T^3$  region of lattice heat capacity must extend only to  $T \lesssim \theta_0/1000$ .

None of the proposed explanations of the decrease is in accord with all features of the experimental results. The agreement of the elastic constants with the calorimetric  $\theta_{0n}$  rather than  $\theta_{0s}$  excludes explanations based on an additional  $T^3$  term in the normal-state heat capacity.

If the decrease in lattice heat capacity is associated with a shift in the frequencies of the thermally excited modes of vibration, those modes with frequencies that correspond to temperatures between approximately 0.05 and 0.7°K must be increased by an average of 5%. Within this interval the shift in frequency must be proportional to frequency in order to give the observed  $T^3$  dependence of the superconducting-state lattice heat capacity, and at higher frequencies the shift must drop rapidly to zero, since the discrepancy in lattice heat capacity disappears at about 1.5°K. Alternatively, the shift may extend to somewhat higher frequencies if it develops only gradually as the temperature is reduced below  $T_c$ . In either case, the very-high-frequency modes must be relatively unaffected, since there can be no large change in zero-point energy, and the very-low-frequency modes can change by at most 1 in  $10^4$  in order to agree with the change in the elastic constants.

A change in lattice zero-points energy of only 1 in  $10^7$  would be equivalent to the energy associated with the discrepancy in lattice heat capacities. However, if such a change is responsible for the discrepancy, it appears that the shift in the high-frequency modes is not related in a simple way to the differences in the elastic constants.

<sup>40</sup> I. O. Kulik, Zh. Eksperim. i Teor. Fiz. **43**, 1489 (1962) [English transl.: Soviet Phys.—JETP **16**, 1052 (1963)].

<sup>41</sup> J. G. Daunt and J. L. Olsen, Phys. Rev. Letters **6**, 267 (1961).