

not move in a hydrogen-like orbit. In many cases the wave function of the ground state of the electron at the impurity will resemble more the wave function of the electron at the impurity in free space<sup>12</sup> than that of a point charge imbedded in a dielectric. However, there exist always excited states, if not the ground state, of the type considered in this paper.

The optical absorption associated with the electron

<sup>12</sup> F. Williams, *J. Chem. Phys.* **19**, 455 (1951).

in a state such as the case (3) considered in this paper, is likely to result mainly from transitions  $1s \rightarrow 2p$ , rather than from transitions to the conduction band. However, the energy difference between the  $2p$  state and the conduction band is rather small, and the formulas derived in this paper may still be of value for an interpretation of optical absorption associated with an electron in a hydrogen-like  $1s$  orbit at a multivalent impurity in ionic crystals.

### Atomic Heat of Indium below 20°K

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A calorimetric technique in which a carbon-composition resistor serves simultaneously as both heater and thermometer has been developed and is described briefly. Using this technique, the atomic heat of indium has been measured in the normal state from 1.7°K to 21.3°K and in the superconducting state from 1.8°K to 3.396°K, the transition temperature in zero magnetic field. Tables of smoothed values are given. A method of deducing the separate lattice and electronic contributions to the heat capacities, based on several empirically and/or theoretically tenable assumptions, has been developed and is described in some detail. This method of analysis, when applied to the indium data, led to the conclusion that a cubic analytic form for the critical magnetic field equation would allow conclusions consistent with all the assumptions but that the more commonly used parabolic form would not. Numerical values are given for the constants involved. The temperature dependence of the Debye characteristic temperature of the indium lattice over the entire range of measurement is shown to follow the theoretically expected behavior.

LOW temperature calorimetric measurements can yield information concerning three problems of fundamental importance in solid state physics: vibrational spectra of crystalline lattices, electronic structure, and superconductivity. Numerous theoretical and experimental investigations have shown that the discrete nature of the crystalline lattice causes significant deviations of its heat capacity from the Debye continuum theory only below about one-tenth the Debye characteristic temperature,<sup>1</sup> i.e., below 30°K or 40°K for most materials. The electronic structure of a material is the basis for theoretical calculations of the heat capacity of its electrons. However, only below about 15°K is the heat capacity of the electrons of sufficient magnitude relative to the lattice contribution to allow a reasonably precise test of any theory.<sup>2</sup> In superconductivity, a difference between the heat capacities in the normal and superconducting states is observed. While no present theory adequately explains this effect, any acceptable theory of superconductivity must eventually predict this difference. Superconductivity occurs among the metallic elements only below 10°K.<sup>3</sup>

In addition, the quantity actually measured in a calorimetric experiment on a solid body is the heat capacity at constant pressure  $C_p$ , while theoretical calculations ordinarily give the heat capacity at constant volume  $C_v$ . Therefore, in comparing theory and experiment, it is necessary to correct  $C_p$  to  $C_v$ . At moderately high temperatures, i.e., room temperature, this correction is of sufficient magnitude to require rather precise accounting but the data necessary for making an accurate calculation are usually not available.<sup>4</sup> At low temperatures, i.e., below 20°K,  $C_p - C_v$  becomes vanishingly small so that only a slight correction, if any, need be made to the measured data to compare with theory.

Calorimetric measurements below 20°K were therefore undertaken. This report describes briefly the experimental technique employed and gives the results obtained on indium. There were several reasons why indium was chosen for investigation. First, there were no useful calorimetric data below room temperature in the literature; second, it is a metallic element and should have at low temperatures a measurable heat capacity due to the conduction electrons; and third, it becomes superconducting at about 3.4°K. Thus information related to all the problems mentioned

<sup>1</sup> M. Blackman, *Repts. Progr. Phys.* **8**, 11 (1941).

<sup>2</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Secs. 27, 28, and 101.

<sup>3</sup> D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), Chap. I and Appendix I.

<sup>4</sup> J. K. Roberts, *Heat and Thermodynamics* (Blackie and Son, Ltd., London, 1940), pp. 161-2.

above may be gained from a calorimetric study of indium. Also, indium has a low melting point and can be easily obtained in a state of high purity so that preparation of a sample was a relatively minor problem.

#### EXPERIMENTAL TECHNIQUE

It can be readily shown that with an electrical heater supplying heat to a body at the rate  $EI$ , under conditions of imperfect thermal isolation, the heat capacity of the body at temperature  $T$  (assuming perfect thermal conductivity) is

$$C_T = EI / (\dot{T}_m - \dot{T}_0), \quad (1)$$

where  $E$  is the voltage drop across the heater,  $I$  the current through it,  $\dot{T}_m$  the time rate of change of temperature when  $EI \neq 0$ , and  $\dot{T}_0$  the time rate of change of temperature when  $EI = 0$ , all quantities to be determined at the temperature  $T$ . Since the measurement of heat capacity intrinsically requires dynamic observations, it is impossible to determine directly all the quantities in Eq. (1) at a single temperature. In the technique described here, a carbon-composition resistor<sup>5</sup> is used simultaneously as both heater and thermometer, the principal observation during a calorimetric experiment being the electrical resistance of this resistor as a function of time. The  $E$  in Eq. (1) is maintained practically constant and the resistance-time data furnishes information for determining  $I$  and  $\dot{T}_m$  directly and  $\dot{T}_0$  indirectly.

The thermometer-heater is cemented into a close-fitting hole along the central axis of a cylindrical specimen of the material to be studied. This sample is suspended in an ordinary vacuum calorimeter, Fig. 1, consisting essentially of a brass can which may be either evacuated for making calorimetric measurements or filled with helium exchange gas for cooling the sample and calibrating the carbon-composition thermometer. The upper part of this can is a vapor pressure thermometer into which a small amount of liquid helium or hydrogen may be condensed.<sup>6</sup> A Wheatstone bridge having equal ratio arms and a three lead connection to the thermometer<sup>7</sup> is used to measure the resistance of the thermometer-heater. By using a dc amplifier whose output is fed into a General Electric photoelectric recorder, as the null detector for this bridge, a permanent record of the unbalance voltage as a function of time is obtained.

For making calorimetric measurements, a bridge voltage is chosen so that the heat developed in the thermometer-heater will cause the sample temperature to rise an amount between 0.05° and 0.5° in 300 seconds

<sup>5</sup> J. R. Clement and E. H. Quinell, Rev. Sci. Instr. 23, 213 (1952).

<sup>6</sup> Temperatures were obtained below 4.2°K from the vapor pressure of liquid helium using the "1949 scale" [H. van Dijk and D. Shoenberg, Nature 164, 151 (1949)] and between 10° and 20°K from the vapor pressure of liquid hydrogen [Wooley, Scott, and Brickwedde, J. Research Natl. Bur. Standards 41, 379 (1948)].

<sup>7</sup> Reference 4, p. 23.

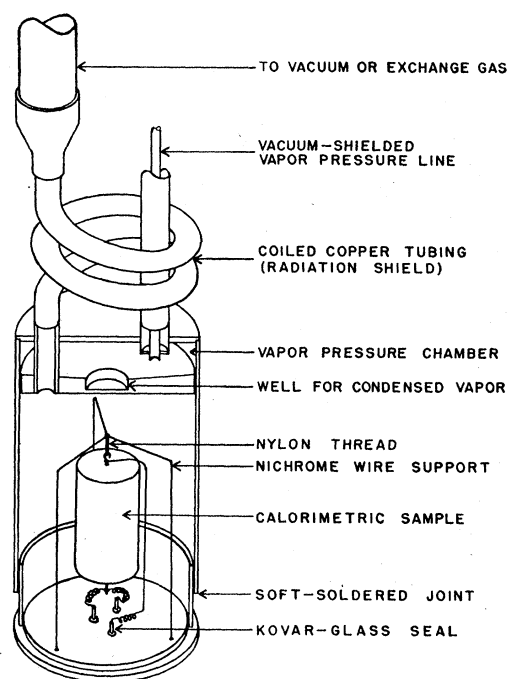


FIG. 1. Sketch of calorimeter can showing principal details of construction and assembly.

depending on the temperature range to be studied. During the 300-second heating period, the balancing resistor of the bridge is changed by fixed increments so that 10 or more resistance nulls are obtained. The values of the balancing resistor at the first and last nulls, as well as the size of the increments, are recorded separately and the exact time of each null can later be read from the recorder chart. At the end of this heating period the bridge voltage is turned off and no measurements made for the next 300 seconds, a "cooling" period. At the end of this "cooling" period another 300 second heating period follows immediately, and this process is continued without interruption until the desired temperature range has been covered. During the experiment, the temperature of the liquid helium surrounding the calorimeter can is maintained very nearly constant.

At the temperature prevailing at the mid-time of the  $n$ th heating period, the quantities in Eq. (1) are presumed to be as follows. First,

$$\dot{T}_{m,n} = (T_{f,n} - T_{i,n}) / (t_{f,n} - t_{i,n}), \quad (2)$$

where  $T_{f,n}$  is the final temperature,  $T_{i,n}$  the initial temperature,  $t_{f,n}$  the time at which heating stopped, and  $t_{i,n}$  the time at which heating began for the  $n$ th heating period, the initial and final temperatures being obtained by extrapolation of a smooth curve through the actual data. In practice, instead of calculating a temperature corresponding to each resistance null, some simple function of resistance, such as  $1/R$  or  $\log R$ ,

TABLE I. Synopsis of calorimetric experiments on indium.

Experimental run	Date	Bridge voltage (volts)	Temperature range (°K)	Magnetic field (gauss)	Cooling times (seconds)	Helium bath temperature (°K)
H	5-9-50	1.50	2.3-3.8	0	300	1.85
J	5-18-50	1.50	1.7-4.3	250	300	1.57
$M_a$	11-2-50	1.92	1.9-3.5	0	300	1.63
$M_b$	11-2-50	1.92	1.8-2.3	0	300	1.59
$M_c$	11-2-50	1.92	1.7-2.4	250	300	1.59
N	9-27-51	2.00	4.5-9.6	0	300	4.21
O	9-27-51	4.00	10.3-13.7	0	150	4.21
P	9-27-51	10.00	17.2-21.3	0	150	4.21
Q	10-4-51	4.00	5.9-19.2	0	200-400	4.21
R	10-5-51	4.00	18.7-21.2	0	200-400	4.21

giving nearly linear curves for the heating periods, is plotted and actual temperatures calculated only for the initial, mid-time, and final resistance values.

The total voltage applied to the resistance bridge  $E_b$  is automatically maintained highly constant so that

$$(EI)_n = [E_b/2]^2 [R_n/(R_n + r_n)^2], \quad (3)$$

where  $R_n$  is the resistance of the thermometer-heater at the mid-time of the  $n$ th heating period and  $r_n$  is the resistance at the time of the  $n$ th heating period of any one of the three (constantan) leads from outside the cryostat to the thermometer. A switching arrangement is incorporated in the bridge so that the series resistance of two of these three leads may be measured during a "cooling" period.

Finally,

$$\dot{T}_0, n = \frac{1}{2} \left[ \frac{T_{i, n} - T_{f, n-1}}{t_{i, n} - t_{f, n-1}} + \frac{T_{i, n+1} - T_{f, n}}{t_{i, n+1} - t_{f, n}} \right], \quad (4)$$

i.e., simply the average of the rate of change of temperature during the "cooling" period just preceding and that just following the heating period under consideration. The time intervals in Eqs. (2) and (4) are independently measured on separate clocks, run by the same power source as the time scale of the General Electric recorder chart, so that they are known to  $\pm 0.1$  second.

If  $\dot{T}_0$  be expanded in a power series of the time, Eq. (4) takes proper account only of the constant and first power term. A simple means of testing whether higher power terms are of sufficient magnitude to influence the results, and also for detecting other possible anomalies in the heat exchange correction, such as excessive heat loss through electrical leads, is to vary the cooling times during a calorimetric run. In the later work on indium, and also that on lead,<sup>8</sup> the cooling times were alternately 200 and 400 seconds, requiring, of course, an appropriate modification of Eq. (4). The  $\dot{T}_0$ 's obtained in these experiments lay on a reasonably smooth curve, when plotted as a function of average

sample temperature, with no systematic difference for the two cooling times, justifying the use of Eq. (4) and indicating that no anomalous effects were contributing to the measured values of  $\dot{T}_0$ .

The over-all validity of the method rests primarily on two assumptions: (1) after the first few seconds, the temperature difference existing radially across the thermometer-heater<sup>9</sup> is essentially constant during the heating period; and (2) the temperature difference which exists radially across the sample during heating is negligibly small compared to the total temperature rise resulting from heating. The validity of these assumptions may be tested by making calorimetric measurements on the same sample over the same temperature range for two, or more, heating rates, i.e., bridge voltages. This was done for the indium data as will be noted later.

A study of these two effects has also been made by means of an electrical analog computer.<sup>10</sup> The results of this study indicated that the temperature difference in the thermometer is determined by the electrical power developed and is essentially independent of time, after a few seconds, if the thermometer is mounted in a sample of any practical size with any likely thermal diffusivity. The study further showed that the linearity of the temperature-time curves while heating, particularly the linearity during the first part of the heating, is an indication of the validity of the assumption (2) above. Therefore, the temperature at the mid-time of each heating period is compared with the average of the initial and final temperatures for that heating period. For each heating period so far analyzed, except those in which the transition from the superconducting to the normal state occurred, the mid-time temperature deviated from the average temperature by less than 1 percent of the total temperature rise for that heating period. Also, each heating period was examined graphically for abnormal curvature during the early portion. If  $\dot{T}_m$  be expanded in a power series of the time, Eq. (2) takes proper account only of the constant and first power term. However, the linearity test shows that no higher terms of any significance occur in  $\dot{T}_m$ .

## EXPERIMENTAL RESULTS

Calorimetric measurements were made on a cylindrical specimen of indium weighing 121.7 grams, cast from metal, obtained from the City Chemical Company, having a stated purity higher than 99.9 percent. Ten successful calorimetric experiments were carried out with this sample, and Table I, a synopsis of these runs, gives the resistance bridge voltage, the temperature range covered, the magnetic field applied externally to the sample, the cooling times employed, and the temperature of the helium bath during the run.

<sup>9</sup> See reference 5, Eq. (3).

<sup>10</sup> V. Paschkis and H. D. Baker, Trans. Am. Soc. Mech. Engrs. 64, 105 (1942).

<sup>8</sup> J. R. Clement and E. H. Quinnell, Phys. Rev. 85, 502 (1952).

In all, 180 data points were obtained in the normal state and 50 in the superconducting state.

Preliminary reports of part of this work have already been given.<sup>11,12</sup> Since the method of calculation used in obtaining the data in the earlier reports was not precisely that outlined in the preceding section, in particular, the thermometer calibration equation<sup>13</sup> was not used, all the data have been recalculated for this report according to the stated procedure. This recalculation changed the previous values slightly and reduced considerably the spread in the data. Table II gives smoothed values of the atomic heat in the normal state from 1.7°K to 21.0°K, and Table III smoothed values of the atomic heat in the superconducting state from 1.8°K to 3.396°K. The data in these tables have been corrected for the heat capacity of the thermometer-heater, estimated from the time required to establish the known temperature difference in it at the beginning of the heating periods. While such an estimate is probably not accurate to much better than 30 percent, the resulting error in the actual heat capacity of the sample is very much smaller since the heat capacity of the thermometer was less than 1 percent that of the sample.

The correction  $C_p - C_v$  has also been applied and was calculated from

$$C_p - C_v = AC_p^2T, \quad (5)$$

$A$  being determined from the melting temperature.<sup>4</sup> Again the correction may not be very exact but is so small compared to the total heat capacity of the sample that the resulting error is negligible.

It is possible in the experimental technique described to obtain the relative uncertainty of each quantity involved in deducing the heat capacities since each

TABLE II. Atomic heat at constant volume of normal indium.

Temp. (°K)	Atomic heat (cal/mole deg)	Temp. (°K)	Atomic heat (cal/mole deg)	Temp. (°K)	Atomic heat (cal/mole deg)
1.7	0.002515	3.2	0.01351	9.0	0.3245
1.8	0.002893	3.3	0.01475	9.5	0.3738
1.9	0.003311	3.396	0.01602	10.0	0.4253
2.0	0.003772	3.6	0.01899	11.0	0.5330
2.1	0.004278	3.8	0.02233	12.0	0.6460
2.2	0.004831	4.0	0.02615	13.0	0.7631
2.3	0.005433	4.5	0.03860	14.0	0.8836
2.4	0.006087	5.0	0.05501	15.0	1.007
2.5	0.006797	5.5	0.07479	16.0	1.134
2.6	0.007563	6.0	0.09840	17.0	1.263
2.7	0.008389	6.5	0.1261	18.0	1.395
2.8	0.009278	7.0	0.1581	19.0	1.529
2.9	0.01023	7.5	0.1944	20.0	1.666
3.0	0.01125	8.0	0.2345	21.0	1.806
3.1	0.01234	8.5	0.2780		

<sup>11</sup> J. R. Clement and E. H. Quinell, National Bureau of Standards Circular 519 (1952), p. 89.

<sup>12</sup> J. R. Clement and E. H. Quinell, Phys. Rev. **79**, 1028 (1950).

<sup>13</sup> Reference 5, Eq. (1).

TABLE III. Atomic heat at constant volume of superconducting indium.

Temp. (°K)	Atomic heat (cal/mole deg)	Temp. (°K)	Atomic heat (cal/mole deg)	Temp. (°K)	Atomic heat (cal/mole deg)
1.8	0.002832	2.4	0.006614	3.0	0.01274
1.9	0.003323	2.5	0.007459	3.1	0.01403
2.0	0.003866	2.6	0.008371	3.2	0.01541
2.1	0.004464	2.7	0.009352	3.3	0.01687
2.2	0.005120	2.8	0.01041	3.396	0.01835
2.3	0.005837	2.9	0.01154		

should, for a single experimental run, ideally give a smooth curve when plotted as a function of average sample temperature. Such plots showed  $EI$  to be smooth to one part in 10 000 or better,  $\dot{T}_m$  to about 2 parts in 1000 with occasional points in excess of this value and  $\dot{T}_0$  to about 5 parts in 100. Since the magnitude of  $\dot{T}_m$  was usually at least 10 times that of  $\dot{T}_0$ , the maximum relative error in heat capacity should be about 0.7 percent. For the data reported here 95 percent of the points deviated less than 1 percent from a smooth curve and a distribution curve of the deviations indicated a standard deviation between 0.3 and 0.4 percent. The smallness of the relative error is due to the high thermometric sensitivity of the carbon-composition resistors, to the precision with which the times of resistance nulls can be taken from the recorder tape ( $\pm 0.2$  second), to the relatively good thermal isolation achieved, and most of all, to the high precision in measuring resistance resulting from the use of the comparatively high voltage needed to heat the calorimetric sample as the measuring voltage of the resistance bridge.

The absolute error is more difficult to evaluate precisely. The temperature differences involved in calculating the heat capacities are rather sensitive to the thermometer calibration equation, and errors in the absolute thermodynamic temperatures are indistinguishable, when one compares theory and experiment, from errors in heat capacity values. However, the use of a temperature difference graph in conjunction with a closely fitting calibration equation reduces the error due to each of these sources to probably less than 0.2 percent. The instrumental error and the error due to the heat capacity of the thermometer-heater are both probably less than 0.3 percent. Thus, if the temperature values are regarded as exact, the absolute uncertainty in the atomic heat values appearing in Tables II and III is probably less than 1 percent.

Of these possible errors in absolute values, that due to the heat capacity of the thermometer-heater is undoubtedly systematic and those due to the thermometer calibration are very likely systematic. Therefore, differences in heat capacities, in particular differences between the heat capacities in the normal and superconducting states, would probably have, due to the small relative error in the data, a much higher accuracy than would be reflected by data consistent

with a 1 percent absolute uncertainty. For this reason, and also in order that the tabulated data would represent the best possible estimate of the accuracy of the results, four significant digits have been given for each value in Tables II and III. So that the roughly constant relative accuracy exhibited by the experimental data could be retained in the smoothed data, the smoothing process was essentially that of smoothing the Debye characteristic temperature and calculating smoothed atomic heats from smoothed characteristic temperatures.

### DISCUSSION OF RESULTS

With these data, one has the opportunity to study the electronic atomic heat, the lattice atomic heat, and the thermodynamics of superconductivity as it relates the atomic heat differences between the normal and superconducting states to the temperature dependence of the magnetic field which just destroys superconductivity. Various methods of empirical analysis<sup>14</sup> have been used in the past to study these three effects, but the results have not always been mutually consistent. A method of analysis has been applied here which seeks results consistent with all the presently accepted ideas concerning these properties. In order to describe the method most efficiently, the principal assumptions involved are stated and discussed briefly below.

#### Assumptions

- (1) The electronic atomic heat in the normal state is

$$C_{e,n} = \gamma T, \quad (6)$$

where  $\gamma$  is a constant at low temperatures. This assumption implies that the lattice and electronic heat capacities are independent and therefore additive, but this implication does not appear susceptible to a purely empirical test, since only the total effect of both the lattice vibrations and the electrons can be measured experimentally. Equation (6) results when Fermi-Dirac statistics is applied to a free electron gas<sup>15</sup> and the existence of a linear term in the low temperature atomic heat of many metallic elements has been demonstrated.<sup>16</sup>

(2) If the Debye characteristic temperature  $\Theta$  is allowed to vary with temperature so that it represents the actual atomic heat of a crystalline lattice, then

$$\lim_{T \rightarrow 0} (d\Theta/dT) = 0. \quad (7)$$

This condition on  $\Theta$  appears to be a generally valid result of investigations of the lattice heat along the lines of the Born-von Kármán lattice dynamics, and it has received empirical support from the results of calorimetric measurements on materials which have

<sup>14</sup> See, e.g., Burton, Grayson-Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Company, New York, 1940), Chaps. 6 and 10.

<sup>15</sup> A. Sommerfeld, *Z. Physik* **47**, 1 (1928).

<sup>16</sup> Reference 14, Chap. 6 and Appendix C.

only a lattice, and no electronic, contribution to the heat capacity.<sup>1</sup> For a three-dimensional lattice, this assumption is equivalent to the condition that a power series representing the heat capacity near 0°K contain no first, second, or fourth power temperature terms.

(3) Below the transition temperature in zero magnetic field, the heat capacity of the lattice is the same function of temperature in the normal and superconducting states. Measurements of the elastic constants<sup>17-19</sup> and the thermal expansion coefficient<sup>20</sup> on passing from one state to the other indicate that any difference in the lattice contributions in the two states is probably less than a few tenths percent and therefore within the experimental error of calorimetric measurements.

(4) No linear temperature term occurs in the atomic heat in the superconducting state. All the available evidence on superconducting elements supports this assumption.<sup>21,22</sup> The evidence considered here is that smooth curves drawn through plots of  $C_{v,s}/T$  versus  $T^2$  appear to extrapolate through the origin of coordinates,  $C_{v,s}$  being the atomic heat in the superconducting state.

(5) Rather early in the study of superconductivity, it was noted that the magnetic field which just destroys superconductivity  $H_c$  varies almost parabolically with temperature.<sup>23</sup> Maxwell<sup>24</sup> has recently shown that the critical field data can be more adequately represented by the addition of a cubic term to the parabola. A convenient form for the cubic equation is

$$H_c = H_0[1 - at^2 + (a-1)t^3], \quad (8)$$

where  $H_0$  is the critical field at 0°K,  $a$  is a numerical constant near unity, and  $t$  is the reduced temperature  $T/T_c$ ,  $T_c$  being the transition temperature in zero magnetic field. Since the cubic form includes the parabola as a special case ( $a \equiv 1$ ), Eq. (8) will be assumed as the analytic form for the critical field curve.

(6) The thermodynamics of superconductivity<sup>25</sup> gives correctly the difference in the atomic heats in the

<sup>17</sup> W. J. de Haas and M. Kinoshita, *Proc. Amsterdam Acad. Sci.* **30**, 598 (1927).

<sup>18</sup> J. R. Clement [U. S. Office of Naval Research Cryogenics Conference, Yale University, 1948 (unpublished)] reported some observations of the elastic constants of tantalum which showed that they remained constant within 0.2 or 0.3 percent on passing from the normal to the superconducting state.

<sup>19</sup> W. C. Overton, Jr. [thesis, Rice Institute, 1950 (unpublished)] measured the elastic properties of tin and tantalum in the liquid helium range by an ultrasonic pulse technique. The moduli of both elements remained constant within 0.1 percent on passing from the normal to the superconducting state.

<sup>20</sup> McLennan, Allen, and Wilhelm, *Trans. Roy. Soc. Can.* **25**, 1 (1931).

<sup>21</sup> Reference 3, pp. 62 and 63.

<sup>22</sup> In one of the preliminary reports of the present data (reference 11), the possible existence of a small linear term in the atomic heat of superconducting indium was proposed. Recalculation of the data changed the absolute values of the atomic heat sufficiently that this conclusion of the earlier report is no longer valid.

<sup>23</sup> W. Tuyn and H. K. Onnes, *J. Franklin Inst.* **201**, 379 (1926).

<sup>24</sup> E. Maxwell, *Phys. Rev.* **86**, 235 (1952).

<sup>25</sup> C. J. Gorter and H. Casimir, *Physica* **1**, 306 (1934).

normal and superconducting states, that is,

$$C_{v,s} - C_{v,n} = [VT/8\pi][d^2(H_c^2)/dT^2], \quad (9)$$

where  $V$  is the atomic volume,  $C_{v,n}$  the atomic heat in the normal state, and the other quantities are as already defined. Many experimental investigations have yielded supporting evidence,<sup>26</sup> although in some cases the lack of agreement between calorimetric and magnetic results appears to be greater than experimental error. Since the heat capacity difference is a function of derivatives of the critical field curve, this lack of agreement may be due to the difficulty in accurately differentiating these curves. Fundamentally, this assumption implies the thermodynamic reversibility of transitions between the normal and superconducting states.

(7) The transition temperature in zero magnetic field can be determined with sufficient exactness from calorimetric and/or magnetic measurements to be taken as a known, unadjustable, quantity in any analysis of data.

A variety of ways to attempt to arrive at conclusions consistent with all these assumptions can be imagined. However, only the particular one finally adopted here will be discussed. Assumptions (1) and (2) applied simultaneously to normal state calorimetric data yield a value, or limits on the value, of  $\gamma$  in Eq. (6). The exact means of applying these two assumptions may vary, a more or less standard procedure being to plot  $C_{v,n}/T$  versus  $T^2$ . If  $\Theta$  is sufficiently constant over the temperature range in which data are available, such a plot will result in a straight line with an intercept equal to  $\gamma$  and a slope simply related to  $\Theta$  for the lattice.

However, for materials with a relatively low value of  $\Theta$ , such as indium,  $\Theta$  may not become constant in the liquid helium temperature range so that erroneous values of  $\gamma$  result from such a procedure. An alternative method which takes account of the variation of  $\Theta$  with  $T$  is suggested by the work of Blackman<sup>27</sup> on simple cubic lattices. He finds that near the absolute zero the heat capacity  $C_L$  of any three-dimensional lattice should become

$$C_L = AT^3 + BT^5, \quad (10)$$

where the constants  $A$  and  $B$  have been used in place of the exact expressions for his particular case.<sup>28</sup> It follows from Eq. (10) that

$$(d/dT)[(C_{v,n} - \gamma T)/T^3] = 2BT. \quad (11)$$

Thus, a plot of the rate of change of  $(C_{v,n} - \gamma T)/T^3$  with  $T$  versus  $T$  should yield, for the correct value of  $\gamma$ , a straight line passing through the origin of coordinates. Figure 2 shows such plots for several values of  $\gamma$ , the plotted points being obtained by graphical differentiation of smooth curves of  $(C_{v,n} - \gamma T)/T^3$  versus  $T$ .

<sup>26</sup> Reference 3, Chap. III.

<sup>27</sup> M. Blackman, Proc. Roy. Soc. (London) **A159**, 416 (1937).

<sup>28</sup> From a purely empirical point of view, Eq. (10) may be interpreted as a theoretical justification for ignoring in the analysis the higher power terms permitted by the less stringent condition, Eq. (7).

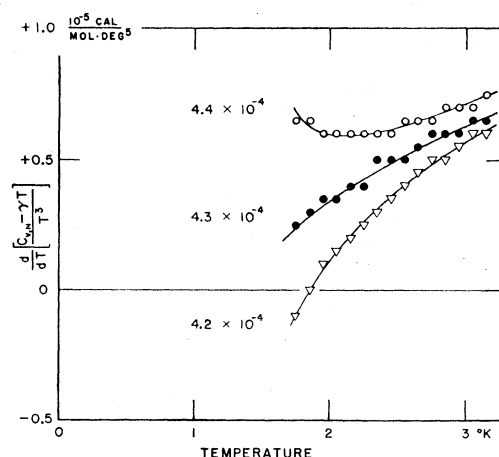


FIG. 2. Graphical application of Blackman's result (lattice heat =  $AT^3 + BT^5$ ) for finding the normal electronic heat,  $\gamma T$ . The  $\gamma$  value associated with each curve is indicated in the figure.

Blackman makes no specific remarks in his paper concerning the temperature range over which Eq. (10) should be applicable. However, for the particular case which he has calculated it appears to be from 0°K up to about  $\Theta/30$  and this range has been assumed valid for the present analysis. The curves in Fig. 2 indicate a value of  $\gamma$  a little greater than  $4.3$ , and certainly between  $4.2$  and  $4.4 \times 10^{-4}$  cal/mole deg<sup>2</sup>. Had indium not been a superconductor, values of  $\gamma$  between  $4.3$  and  $4.4 \times 10^{-4}$  would have been tried to find the most likely value. In this case, however, we seek results as consistent as possible with all the assumptions so we take only the outside limits on  $\gamma$  and continue the analysis to find if any value within these limits is consistent with the other assumptions.

Assumptions (5) and (6) yield the result that

$$C_{v,s} - C_{v,n} = [VH_0^2 T / 4\pi T_c^2] [15(a-1)^2 t^4 - 20a(a-1)t^3 + 6a^2 t^2 + 6(a-1)t - 2a]. \quad (12)$$

Assumptions (1), (3), and (4) lead then to the following identification of terms in Eqs. (6) and (12),

$$\gamma = aVH_0^2 / 2\pi T_c^2. \quad (13)$$

Using this result, it is possible to rearrange Eq. (12) in the following form,

$$\frac{2(C_{v,s} - C_{v,n})}{\gamma T (15t^4 - 20t^3 + 6t^2)} + \frac{15t^4 - 20t^3 + 2}{15t^4 - 20t^3 + 6t^2} = a - \alpha \left[ \frac{15t^4 - 6t}{15t^4 - 20t^3 + 6t^2} \right], \quad (14)$$

where

$$\alpha = 1 - (1/a). \quad (15)$$

According to the definition of  $\alpha$  in Eq. (15), Eq. (14) really involves two constants,  $\gamma$  and  $a$ , which are to be determined. However, Eq. (14) is quadratic in  $a$ , and

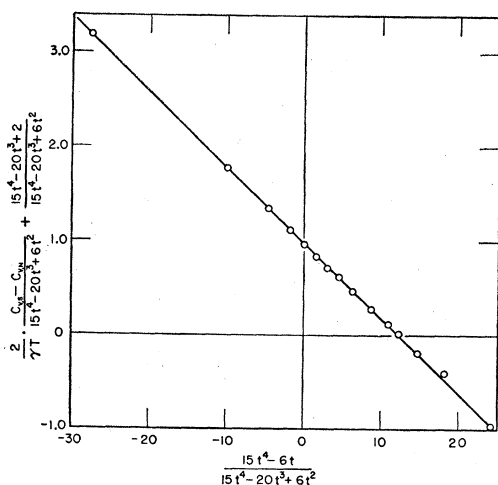


FIG. 3. Illustration of the method of determining  $a$  and  $\alpha$  in Eq. (14), for the case  $\gamma = 4.2 \times 10^{-4}$  cal/mole deg<sup>2</sup>.

no simple direct means could be found for evaluating the best values of these two constants. A rather convenient method which was used, and which has the advantage that both calorimetric and magnetic results can be compared in a single graph, is as follows. We suppose that Eq. (14) actually contains three constants,  $\gamma$ ,  $a$ , and  $\alpha$ . We choose a value for  $\gamma$  from the limits already determined from the normal state calorimetric data and evaluate  $a$  and  $\alpha$  by the straight line graph method, which means that we plot the entire left side of Eq. (14) as a function of the bracketed portion on the right side. One such graph, for  $\gamma = 4.2 \times 10^{-4}$  cal/mole deg<sup>2</sup>, is shown in Fig. 3. The points plotted in this figure were obtained from the differences in smoothed calorimetric data, and a point is included for each 0.1° interval between 1.8°K and 3.396°K. We now define, for a particular value of  $\gamma$ , two values of  $a$  in terms of the constants of the straight line like that in Fig. 3. One of these,  $a(0)$ , is the intercept of the line, and the other,  $a(\alpha)$ , results from substituting the slope of the line,  $\alpha$ , into Eq. (15) and solving for  $a(\alpha)$ . After carrying out this procedure for several values of  $\gamma$ , curves can be constructed showing the dependence of  $a(0)$  and  $a(\alpha)$  on  $\gamma$ , and from the crossing point of these curves, if one exists, the set of values of  $\gamma$  and  $a$  which satisfy Eq. (14) can be found. Figure 4 shows such curves and yields the values,  $\gamma = 4.33 \times 10^{-4}$  cal/mole deg<sup>2</sup> and  $a = 1.105$ .

The fact that the curves in Fig. 4 have a crossing point within the range of  $\gamma$  values obtained from the normal state data means that assumptions (2) and (3) can be satisfied with the values of  $a$  and  $\gamma$  indicated by the crossing point. However,  $a$  and  $\gamma$  also determine the critical field curve and it is not necessarily true that the crossing point of the  $a(0)$  and  $a(\alpha)$  curves will give a curve in agreement with magnetic data. Therefore, a shaded area has also been included in Fig. 4. This area represents the range of values of  $a$  and  $\gamma$

which can, within the spread in the existing data,<sup>29-31</sup> give critical field curves in agreement with experiment. The extent of this area was determined by drawing, for several values of  $a$  included on the curve, straight lines with reasonable maximum and minimum intercepts through plots of  $H_c/(1-t^3)$  versus  $(t^3-t^2)/(1-t^3)$ . Such curves have intercepts equal to  $H_0$  and slopes equal to  $aH_0$ . The maximum and minimum values of  $H_0$  so determined were then substituted into Eq. (13) and the maximum and minimum values of  $\gamma$  calculated. From such a composite of experimental data as contained in Fig. 4 a set of values of  $a$  and  $\gamma$  which will be most nearly consistent with all the assumptions may be chosen. Since, in this particular case, the crossing point of the  $a(0)$  and  $a(\alpha)$  curves is within the shaded area, the exact values of  $a$  and  $\gamma$  at that point were used.

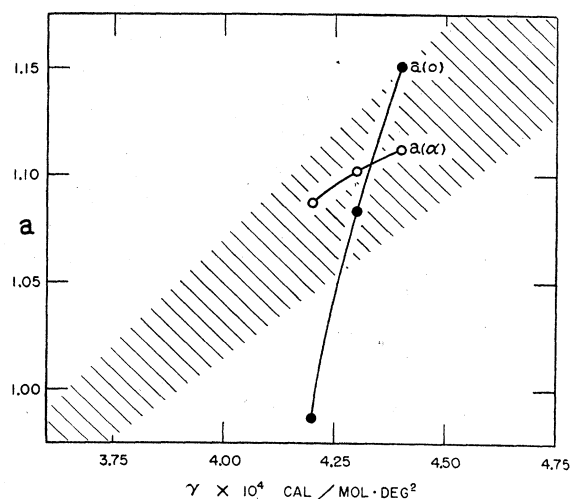


FIG. 4. Composite of experimental data for finding the values of  $a$  and  $\gamma$  most nearly consistent with the assumptions that  $\Theta \rightarrow 0^\circ\text{K}$ , the lattice heat is independent of the magnetic state, and transitions between the normal and superconducting states are thermodynamically reversible. The two curves,  $a(0)$  and  $a(\alpha)$ , result from calorimetric data and the shaded area from magnetic data.

To carry out the analysis just described, numerical values for  $T_c$  and  $V$  were necessary. In two calorimetric runs on the indium sample, the transition from the superconducting to the normal state was observed with the sample in the earth's magnetic field. In both cases, the  $T_c$  value obtained was  $3.390 \pm$  about  $0.005^\circ\text{K}$ . Correcting for the earth's field, we get  $T_c = 3.396 \pm 0.005^\circ\text{K}$ . The transition of the sample was also determined magnetically by measuring the inductance of a coil wound directly on the sample as a function of temperature. This experiment gave a transition of  $3.390^\circ\text{K}$  in the earth's field and also results in a zero field transition of  $3.396^\circ\text{K}$ . The recent work of Stout

<sup>29</sup> J. W. Stout and L. Guttman, Phys. Rev. **88**, 703 (1952).

<sup>30</sup> Daunt, Horseman, and Mendelssohn, Phil. Mag. **27**, 754 (1939).

<sup>31</sup> A. D. Misener, Proc. Roy. Soc. (London) **A174**, 262 (1940).

and Guttman<sup>29</sup> on the critical fields of indium and indium-thallium alloys gave a zero field transition for pure indium of 3.396°K, that of Daunt *et al.*<sup>30</sup> on indium gave 3.4° and that of Misener<sup>31</sup> gave 3.386°K. The most likely value of  $T_c$  appears to be 3.396°K, and this value has been used throughout the analysis.

The  $V$  appearing in Eqs. (9), (12), and (13) should be the atomic volume at and below  $T_c$ . Since the thermal expansion vanishes, as required by the third law of thermodynamics, as the temperature approaches absolute zero, the atomic volume needed is simply that at absolute zero. The atomic volume at ordinary room temperatures, calculated from density<sup>32,33</sup> and x-ray crystallographic<sup>34-36</sup> measurements, ranges between 15.61 cm<sup>3</sup> and 15.76 cm<sup>3</sup>, the most likely value being 15.76 cm<sup>3</sup>. Using the rather meager and conflicting data available on the thermal expansion of indium,<sup>33</sup>

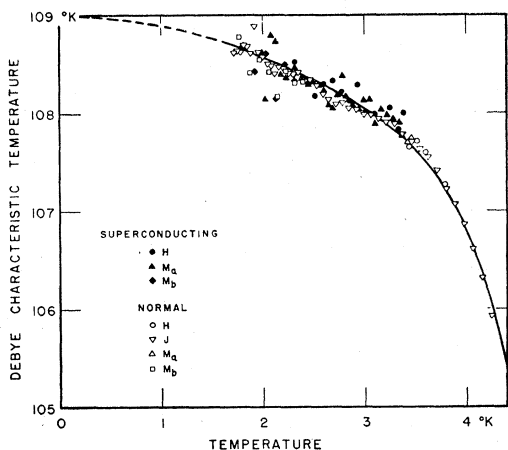


FIG. 5. Graphical test of compliance of the calorimetric data with the assumptions that  $\Theta \rightarrow \text{constant}$  as  $T \rightarrow 0^\circ\text{K}$ , the lattice heat is independent of the magnetic state, and the electronic heats may be deduced thermodynamically from a critical field equation of cubic analytic form. The legend in the figure identifies the experimental run (see Table I) in which the data were obtained.

with the Grueneisen<sup>37</sup> thermal expansion formula as an aid in extrapolating the data, the fractional change in volume between room temperature and the absolute zero is found to be between 0.020 and 0.037, the most likely value being about 0.027. From these data the atomic volume at 0°K should lie somewhere between 15.03 cm<sup>3</sup> and 15.45 cm<sup>3</sup>. The most likely value appears to be 15.33 cm<sup>3</sup>, and this value has been used in the present analysis.

<sup>32</sup> *Handbook of Chemistry and Physics* (Chemical Rubber, Cleveland, 1947), 30th edition, p. 1686.

<sup>33</sup> P. Hidnert and M. G. Blair, *J. Research Natl. Bur. Standards* **30**, 427 (1943).

<sup>34</sup> Reference 32, p. 2016.

<sup>35</sup> L. K. Frevel and E. Ott, *J. Am. Chem. Soc.* **57**, 228 (1935).

<sup>36</sup> L. Guttman, *J. Metals* (Trans. Am. Inst. Mining Met. Engrs.) **188**, 1472 (1950).

<sup>37</sup> E. Grueneisen, *Handbuch der Physik* (J. Springer, Berlin, 1926), Vol. 10, p. 1.

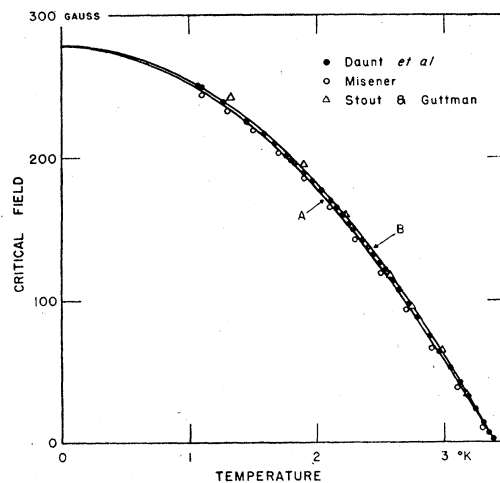


FIG. 6. Comparison of the experimental magnetic field data with two analytic curves deduced from calorimetric data. Curve A is the cubic form which corresponds to the results presented in Fig. 5 and curve B is the parabolic form which corresponds to the results presented in Fig. 7.

While Fig. 4 shows that  $a$  and  $\gamma$  can be chosen to give agreement with assumptions (2) and (3), it does not show directly how exact this agreement may be. For a more detailed examination, it is necessary to subtract the electronic atomic heats from the measured values for both the normal and superconducting states and compare the two Debye characteristic temperatures of the resulting lattice heats. Equations (12) and (13) lead to the conclusion that the electronic heat in the superconducting state  $C_{e,s}$  is

$$C_{e,s} = (\gamma T/2a)[15(a-1)^2 t^4 - 20a(a-1)t^3 + 6a^2 t^2 + 6(a-1)t]. \quad (16)$$

Using Beattie's<sup>38</sup> tabulated values of the Debye specific heat function, with  $3R = 5.960$  cal/mole deg,  $\Theta$  values were calculated for each data point in the normal state after subtracting the normal electronic heat as given by Eq. (6) and for each point in the superconducting state after subtracting the value calculated according to Eq. (16), the constants being  $\gamma = 4.33 \times 10^{-4}$  cal/mole deg<sup>2</sup>,  $a = 1.105$  and  $T_c = 3.396^\circ\text{K}$ . Figure 5 shows the results with the data from the different experimental runs distinguished from each other. Both assumptions (2) and (3) are seen to be satisfied within experimental error and the agreement between the data for different heating rates is evident.

Figure 4 also indicates that there will be some semblance of agreement between the measured critical field data and the cubic curve deduced from the chosen values of  $a$  and  $\gamma$ . However, there is even less indication in this case than in the preceding one of how exact this agreement may be. Figure 6 shows the data of Stout and Guttman,<sup>29</sup> Daunt *et al.*,<sup>30</sup> and Misener,<sup>31</sup> together with two smooth curves deduced directly from

<sup>38</sup> J. A. Beattie, *J. Math. and Phys.* **6**, 1 (1926-1927).



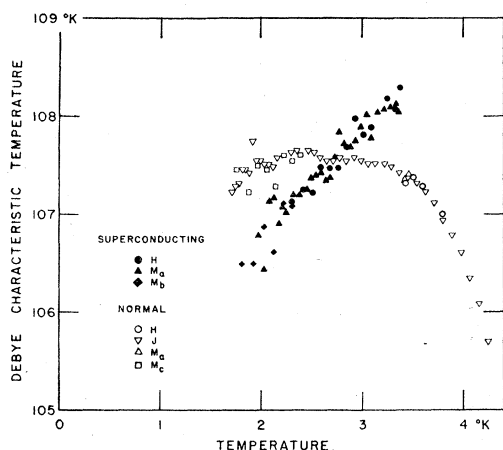


FIG. 7. Graphical test of compliance of the calorimetric data with the assumptions that  $\Theta \rightarrow \text{constant}$  as  $T \rightarrow 0^\circ\text{K}$ , the lattice heat is independent of the magnetic state, and the electronic heats may be deduced thermodynamically from a critical field equation of parabolic analytic form. The legend in the figure identifies the experimental run (see Table I) in which the data were obtained.

the calorimetric data. Curve A is calculated from Eq. (8) with  $H_0 = 278.4$  gauss,  $a = 1.105$ , and  $T_c = 3.396^\circ\text{K}$ . The value of  $H_0$  results from substituting numerical data into Eq. (13). The measured values of Daunt *et al.* are rather close to this smooth curve while the other two sets of data fall on either side. Some uncertainty is present in the smooth curve because of uncertainty in the low temperature atomic volume. Based on the estimated uncertainty in the atomic volume noted above, however, the uncertainty in the critical field curve from this source should not exceed 1 percent.

One difficulty in the foregoing analysis is that it provides no indication of how well the several assumptions can be satisfied if the parabolic form of the critical field curve is used in place of the more flexible cubic form. From Fig. 4 it is apparent that some agreement between the critical field data and a parabolic curve can be obtained with  $\gamma$  values between  $3.65 \times 10^{-4}$  and  $3.90 \times 10^{-4}$  cal/mole deg<sup>2</sup>. However, Fig. 2 shows that  $\gamma$  must be considerably higher than the highest of these values to be in agreement with assumption (2). The possibility of satisfying assumption (3) was investigated by calculating the lattice  $\Theta$ 's for the normal and superconducting states after subtracting the appropriate electronic atomic heats given by Eqs. (6) and (16) with  $a \equiv 1$ ,  $T_c = 3.396^\circ\text{K}$  and  $\gamma$  values of 3.65, 3.90, and  $4.33 \times 10^{-4}$  cal/mole deg<sup>2</sup>. In no case was assumption (3) satisfied even approximately within experimental error. The results obtained with  $\gamma = 3.90 \times 10^{-4}$  cal/mole deg<sup>2</sup>, the value most nearly consistent with both calorimetric data and a parabolic critical field curve, are shown in Fig. 7. The appearance of the data for  $\gamma = 4.33 \times 10^{-4}$  was somewhat similar, the superconducting state data having about the same slope

relative to the normal state data but crossing the normal data at a lower temperature. Curve B of Fig. 6 is the parabolic curve calculated from Eq. (8) with  $H_0 = 278.3$  gauss and  $a \equiv 1$ . This value of  $H_0$  results from substituting numerical data into Eq. (13),  $a \equiv 1$ ,  $T_c = 3.396^\circ$ ,  $\gamma = 3.90 \times 10^{-4}$  cal/mole deg<sup>2</sup> and  $V = 15.33$  cm<sup>3</sup>.

Figures 5 and 7 form a dramatic illustration of the sensitivity of the derived electronic heat capacities to the shape of the critical field curve. So far as the magnetic data are concerned, curve A, the cubic, and curve B, the parabola, of Fig. 6 are essentially the same. However, when thermodynamics is applied to these equations to obtain the electronic heats, the calorimetric results are remarkably different as shown by comparing Fig. 5, the results of the cubic curve, with Fig. 7, the results of the parabolic curve.

Finally, the temperature dependence of the Debye characteristic temperature of the lattice over the entire temperature range of measurement may be compared with theoretical results when the discrete nature of the lattice is taken into account in calculating a vibration spectrum. Generally, these calculations have resulted in qualitatively similar curves,<sup>1,27</sup> having the following principal features in the temperature range for which indium data are available.  $\Theta$  starts from some roughly constant value near  $0^\circ\text{K}$ , drops with rising temperature, passes through a minimum, then rises again with further increase in temperature to some other value which may, or may not, represent a maximum. Indium crystallizes in the face-centered tetragonal structure so that no existing calculations can be applied in any quantitative manner. However, Fig. 8, a plot of  $\Theta$  versus  $T$  for indium, shows that the variation of  $\Theta$  with  $T$  follows the general behavior outlined above. The agreement between data obtained with different heating rates is apparent. It might also be noted that the  $\Theta$  curve extrapolates, as indicated in Fig. 5, to  $109.0^\circ\text{K}$  at the absolute zero, the absolute uncertainty in this extrapolated value being perhaps  $\pm 0.3^\circ\text{K}$ .

#### SUMMARY

A calorimetric technique employing a carbon-composition resistor simultaneously as both heater and thermometer was developed. The principal observations during a calorimetric experiment, the time dependence of the resistance of this thermometer-heater, are automatically recorded. Heat capacities are deduced from the initial data by a time derivative method, and criteria for testing the validity of the method on the basis of results of a single run were given.

Using this technique, the atomic heat of indium was measured in the normal state from  $1.7^\circ\text{K}$  to  $21.3^\circ\text{K}$  and in the superconducting state from  $1.8^\circ\text{K}$  to  $3.396^\circ\text{K}$ , the transition temperature in zero magnetic field. The results exhibited a high degree of consistency, the standard deviation of the data from a smooth curve

being between 0.3 and 0.4 percent. Tables of smoothed values were given, the absolute uncertainty in the tabulated values being probably less than 1 percent.

A method of deducing the separate lattice and electronic contributions to the heat capacities, based on several empirically and/or theoretically tenable assumptions was developed. Among these assumptions were that the Debye characteristic temperature of the lattice approaches a constant as the temperature approaches the absolute zero, the lattice heat of a superconductor is independent of the magnetic state, the heat capacity of a superconductor has no linear temperature term, and the equation of the critical magnetic field is of cubic analytic form. The method

TABLE IV. Low temperature physical constants of indium.

Constant	Numerical value
$\gamma$	$4.33 \times 10^{-4}$ cal/mole deg <sup>2</sup>
$a$	1.105
$T_c$	3.396°K
$V$ (0°K)	15.33 cm <sup>3</sup>
$H_0$	278.4 gauss
$\Theta$ (0°K)	109.0°K

of analysis was applied to the indium data and yielded conclusions consistent with all the assumptions. The numerical values of several constants deduced for, or resulting from, this analysis are collected in Table IV. It was further demonstrated that such mutually consistent conclusions could not be found if a parabolic form for the critical field equation was assumed, even though the parabola used was in essentially as good agreement with critical field data as the cubic curve.

Finally, the temperature dependence of the Debye characteristic temperature of the lattice over the entire range of measurement was shown to be in qualitative agreement with that which would be expected on the basis of the few existing calculations which take more

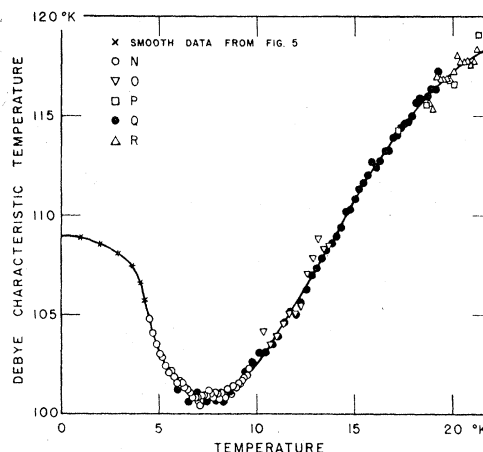


FIG. 8. Curve showing the variation of  $\Theta$  of the indium lattice with  $T$  over the entire range of measurement. The legend in the figure identifies the experimental run (see Table I) in which the data were obtained.

complete account of the discrete nature of the crystalline lattice than the Debye continuum theory.

The authors wish to express their appreciation to the various members of the Cryogenics Branch of this Laboratory, in particular to R. L. Dolecek, J. R. de Launay, M. F. M. Osborne, and R. T. Webber, for many helpful discussions during the course of this investigation.

*Note added in proof:*—Since the completion of this report, the results of some calorimetric measurements on indium between 12°K and 273°K [K. Clusius and L. Schachinger, *Z. angew. Physik* 4, 442 (1952)] have come to the authors' attention. The two sets of data are in good agreement at about 21°K but gradually deviate from each other with decreasing temperature, becoming finally 4 to 5 percent different at about 12°K, the data of Clusius and Schachinger being the higher.

The actual experimental data on which the present report was based are contained in Naval Research Laboratory Document No. 106435 (August 1953).