Heat Capacity of Aluminum between 0.1°K and 4.0°K*

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(Received December 1, 1958)

Measurements of the heat capacity of aluminum have been made between 0.11 and 4.0°K in the normal state and between 0.17 and 4.0°K in the superconducting state. Within the experimental error the normal state heat capacity, C_n, can be represented by $C_n = \gamma T + \beta T^3$ with $\gamma = 1.35 \times 10^{-3}$ Joules/mole deg^2 and a value of β corresponding to a Debye temperature of 427.7° in agreement with calculations based on elastic constants. For reduced temperatures between 0.5 and 0.25 the electronic heat capacity in the superconducting state, C_{es}, is approximated by $C_{es}/\gamma T_c = 7.1 \exp(-1.34\, T_c/T)$, in which T_c is the transition temperature, 1.163°K. At reduced temperatures less than about 0.25, C_{es} is greater than an extrapolation of the exponential, the difference amounting to a factor of 4 at the lowest temperature. The departure of C_{es} from an exponential temperature dependence, which is believed to be outside the experimental error, is not consistent with the existence of a constant energy gap at low reduced temperatures. The calculated critical field is 103.0 gauss at 0°K and shows a maximum negative deviation of 4% from the parabolic law. The results are compared with other measurements and with theory.

I. INTRODUCTION

THE relatively small heat capacity associated with the lattice vibrations of solids at temperatures near and below 1°K makes this region interesting in connection with an evaluation of the contribution of the conduction electrons to the heat capacity of metals. There have been many heat capacity measurements on both normal and superconducting metals in the temperature range 1° to 4°K, which is accessible with liquid helium techniques, but until recently no measurements in the adiabatic demagnetization range had been made. Heat capacity measurements on superconducting aluminum at temperatures below 1°K were undertaken because they would make available data covering an unusually wide range of reduced temperatures. Normal state measurements were also made and the measurements were extended through the liquid helium range to permit a more careful study of the transition region near 1.2°K and to obtain a more accurate evaluation of the normal state parameters than was possible from the measurements below 1°K. Preliminary results of this investigation have already been presented[1] and similar measurements on the superconducting state have been reported by Goodman.[2]

At sufficiently low temperatures the normal state heat capacity C_n is generally considered to be the sum of an electronic and a lattice heat capacity, which are proportional to the first and third powers of the temperature, respectively.[3]

$$C_n = \gamma T + (12/5)\pi^4 R (T/\theta)^3. \qquad (1)$$

In this expression R is the gas constant, T is the tem-

perature, θ is the Debye characteristic temperature of the lattice vibrations and γ is a constant which is proportional to the density of states at the Fermi surface and which may depend on electron correlations[4] and the electron-phonon interaction.[5]

The electronic heat capacity of superconductors can be expected to yield information on the nature of the superconducting state; in particular, its temperature dependence should be related to the energy gap which is a feature of current theories.[6] The treatment of Bardeen, Cooper, and Schrieffer[7] gives an electronic superconducting state heat capacity, C_{es}, which is, for temperatures well below the critical temperature T_c, an exponential function of temperature,

$$C_{es}/\gamma T_c = a e^{-bT_c/T}, \qquad (2)$$

in which the constants a and b are the same for all superconductors. Measurements at temperatures below 1°K are of particular interest as a test of this relation because those metals which show the properties associated with the ideal superconducting state, the soft superconductors, and which have transition temperatures appreciably greater than 1°K, also have relatively large lattice heat capacities. For example, for tin, indium, thallium, and lead, with transitions at 3.7, 3.4, 2.4, and 7.2°K, the lattice heat capacities in the superconducting state at the transition temperature amount to 45%, 77%, 83% and 94% of the respective total heat capacities. On the other hand, some of the soft superconductors with lower transition temperatures have relatively small lattice heat capacities: the corresponding ratios for aluminum, zinc, and cadmium, with transition temperatures 1.2, 0.8 and 0.5°K, are 1%, 3%, and 3%, respectively.

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

[1] N. E. Phillips, *Proceedings of The Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957*, edited by J. R. Dillinger (The University of Wisconsin Press, Madison, 1958).

[2] B. B. Goodman, Compt. rend. 244, 2899 (1957).

[3] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition, pp. 141–144.

[4] D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

[5] M. J. Buckingham and M. R. Schafroth, Proc. Phys. Soc. (London) A67, 828 (1954).

[6] N. Bernardes, Phys. Rev. 107, 354 (1957).

[7] Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

II. APPARATUS AND PROCEDURE

General Description

Figure 1 shows the apparatus as used for measurements in the adiabatic demagnetization range. Temperatures between 1.1°K and 0.1°K were obtained by the adiabatic demagnetization of copper potassium sulfate. Thermal contact to the salt pill was made by molding the powdered salt under pressure onto a system of thin copper vanes attached to a copper wire. The aluminum sample was supported by threads inside a copper shield which was thermally connected to the salt pill. All electrical leads were placed in thermal contact with the shield before being led to the sample and included lengths of 0.0015-in. manganin wire tinned with

TO MANOMETERS

TO DIFFUSION PUMP

STEEL WIRES

VAPOR PRESSURE THERMOMETER

SUPER-CONDUCTING SWITCH

SOLENOID

COPPER ROD

RADIATION TRAP

ELECTRICAL LEADS

COPPER WIRES

FIXED PIVOT

MECHANICAL HEAT SWITCH

HELIUM DEWAR

NITROGEN DEWAR

COPPER TUBE

SOLENOID

METAL SPECIMEN

LUCITE TUBE

PARAMAGNETIC SALT

MAGNET POLE PIECES
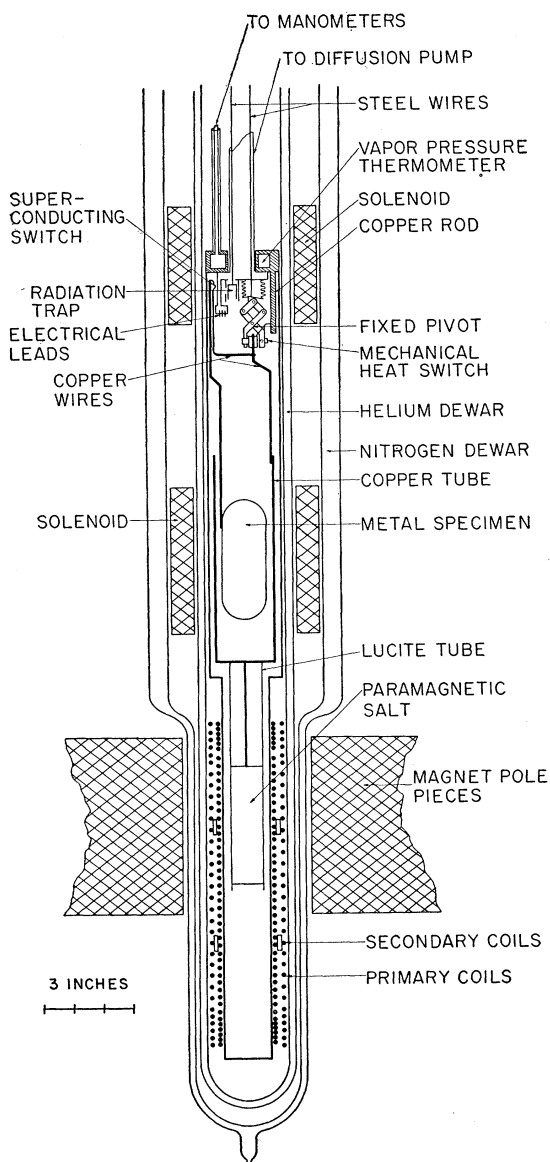
3 INCHES

SECONDARY COILS

PRIMARY COILS

FIG. 1. The apparatus.

soft solder to provide a high thermal resistance without increasing the electrical resistance. Thermal contact between the aluminum sample and the salt pill was controlled by a superconducting thermal switch of either tin or lead, one side of which was soldered to a strip of copper foil which was in turn attached to the sample with General Electric 7031 varnish.[8] Thermal contact between the salt pill and the bulb of a vapor pressure thermometer was made and broken by closing and opening a mechanical heat switch.

The temperature of the sample was measured with a carbon resistance thermometer consisting of a thin layer of Aquadag painted onto a Formex insulated copper wire and connected to the sample by the same method used for the attachment of the superconducting switch. The thermometer voltage was compared with a voltage taken from a potentiometer and the difference was amplified and recorded on a recording potentiometer.

Heat was supplied to the sample by a manganin resistance heater wound directly on the surface and held in place with varnish. The duration of a heating period was read from a clock which was turned on and off by a relay that also controlled the heater power and generated a signal to mark the beginning and end of the heating period on the recording potentiometer chart. The clock was driven by a tuning-fork-controlled oscillator and was capable of measuring the time interval during which the heater circuit was energized with an accuracy of one millisecond.

During an experiment the vacuum jacket containing the salt pill and sample was completely closed to eliminate heat input from radiation or hot gas molecules entering through the pumping tube. The electrical leads were introduced through glass-Kovar seals, the wire for the operation of the mechanical heat switch was sealed to the jacket with a flexible metal bellows, and the pumping tube itself was closed at its lower end by the action of a metal plunger.

At the beginning of an experiment the system was cooled from room temperature to 4.2°K without using helium exchange gas at any time. The susceptibility of the salt was calibrated against the vapor pressure of liquid helium at about twelve temperatures between 4.2°K and 1.1°K with the mechanical switch closed. The salt was magnetized at 1.1°K and, after allowing about thirty minutes for the heat of magnetization of the 200-g salt pill to be conducted away, the mechanical switch was opened and the salt demagnetized. With the superconducting switch closed the carbon resistance thermometer was calibrated against the susceptibility of the salt at about thirty points between 0.1°K and 1.2°K. Between successive calibration points the temperature of the salt pill was raised by supplying power to a heater attached to it. About two minutes were required to obtain thermal equilibrium between the salt pill and the thermometer following each heat input at

[8] Wheatley, Griffing, and Estle, Rev. Sci. Instr. 27, 1070 (1956).

the lowest temperatures. The total heat leak to the system while the calibration points were being taken was about 100 erg/min. The temperature T and the resistance R were represented to within 1% by $T^{-1}=A+B \log^{-1}R+C \log R+D \log^3 R$, in which A, B, C, and D are constants. A calibration curve giving the ratio of the actual temperature to that calculated from the equation was constructed from the calibration points and used in computing the temperature from the resistance.

Following a second demagnetization, the superconducting switch was opened to leave the aluminum sample thermally isolated from the salt pill and heat capacity measurements were made in the usual way. Before the salt pill warmed up appreciably, it was possible to make several series of measurements covering a range of a few tenths of a degree. The aluminum sample was returned to its original temperature at the end of each series by closing the superconducting switch, and when measurements in that temperature range were complete the temperature of the salt pill was increased and the process repeated.

Measurements at liquid helium temperatures were made with the mechanical switch providing thermal contact between the sample and the vapor pressure bulb. The resistance thermometer was calibrated directly against the vapor pressure of liquid helium at twenty-five points between 1.1°K and 4.2°K.

Typical heating curves are shown in Fig. 2. The temperature increments were calculated by extrapolating the initial and final temperature drifts to the middle of the heating period.

Mechanical Heat Switch

The mechanical heat switch consisted of two copper jaws which were connected to the vapor pressure bulb by flexible copper wires and which could be closed on a central copper wire. The jaws were held normally open by a spring and were closed by a system of levers actuated by applying tension to a steel wire that passed through the pumping tube to an adjusting screw at the top of the cryostat. Webb and Wilks[9] have used a similar mechanical contact but the operating characteristics of the two are different.

When a force of approximately 10 pounds had been applied to the jaws before the system was cooled down, the total thermal resistance between the salt pill and the vapor pressure bulb at 4.2°K and 1.3°K was 500 and 2500 deg/watt, respectively. It was estimated that most of the thermal resistance was at the mechanical contact itself. The first time the jaws were opened and closed at helium temperatures the resistance increased by a factor of about three and remained constant thereafter. No direct measurements of the thermal resistance at higher temperatures were made but it was possible

⁹ F. J. Webb and J. Wilks, Proc. Roy. Soc. (London) A230, 549 (1955).

to cool the 8-mole sample of aluminum from room temperature to 4.2°K in the time ordinarily used to cool down the rest of the apparatus and about ½ hour was required to cool the sample from 20°K to 4.2°K.

When the switch was opened, small increases in the sample temperature were observed which corresponded to heat inputs between a minimum of 20 ergs and as much as several hundred ergs. Undoubtedly part of the heat input is generated by friction between the jaws and the central wire but, since the heat input continued as the jaws were opened beyond the point at which contact with the central wire was broken, it appears that some of the heat was generated by vibrations in the sample suspension induced by operation of the adjusting screw. As might be expected, the heat inputs were a minimum for light samples which were rigidly supported.

The mechanical heat switch has a number of advantages over the helium exchange gas, which it replaces, particularly for adiabatic demagnetization experiments. It removes a major source of heat leak, gas conduction, which would be especially serious for the small heat capacity in the superconducting state at low temperatures and it eliminates errors associated with the desorption of adsorbed helium during a heating period. In addition, the mechanical switch makes it possible to extend the measurements to 1°K or above, through the temperature range in which outgassing of the adsorbed helium from the salt pill would otherwise spoil the insulating vacuum.

Temperature Measurements

Temperatures in the liquid helium region were based on the measurement of helium vapor pressures. Above 2°K the pressure was measured in a vapor pressure bulb
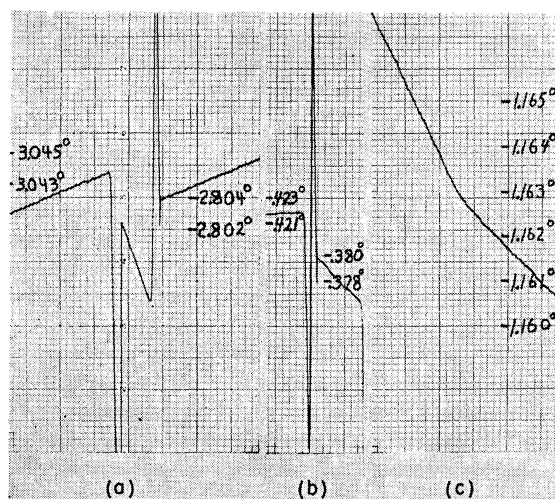

FIG. 2. Typical heating curves. (a) Heat capacity point in the liquid helium region. The outer abrupt changes in slope occur at the beginning and end of the heating period; the others are produced by changing the amplifier gain or potentiometer voltage. (b) Heat capacity point in the adiabatic demagnetization region. (c) Heating curve through the superconducting transition at constant power.

with a vacuum-jacketed, thin-walled, stainless steel tube. A radiation trap consisting of four metal disks with offset holes was inserted at the lower end of the tube. Below 2°K the pressure over the helium bath was measured at a point just below the top of the vacuum jacket of the helium Dewar. The use of two different methods was dictated by the uncertainty of corrections for hydrostatic head at temperatures above the λ-point and thermomolecular pressure gradients at low temperatures.

Temperatures in the adiabatic demagnetization region were based on an extrapolation of the susceptibility of copper potassium sulfate according to a Curie-Weiss law. It can be inferred both from direct measurements of the properties of this salt[10] and from indirect evidence[11] that the temperature derived in this way is a good approximation to the thermodynamic temperature. In practice the mutual inductance, M, of a set of coils surrounding the salt pill was measured with a 23-cycle/sec mutual inductance bridge[12] and M was related directly to the temperature by the expression

$$M = A + B/(T - \Delta) \tag{3}$$

The constants A, B, and Δ were determined by plotting M vs $(T - \Delta)^{-1}$ for the calibration points between 1.1°K and 4.2°K. The value of Δ used in the extrapolation was that for which the best straight-line fit was obtained, 0.033°K.

The primary of the mutual inductance coils was designed to give a uniform field over the salt pill but a small field outside the coils. The secondary was in two parts, one coil at the center of the salt pill and a bucking coil below, each of which was about one-sixth of the length of the salt pill. The coil geometry together with the small susceptibility of copper potassium sulfate reduced to a negligible amount the effect of the non-ellipsoidal shape of the salt pill on susceptibility measurements and also minimized the nonlinearity associated with the presence of metal near the coils.

Apart from the validity of the assumptions inherent in Eq. (3), the calibration of the resistance thermometer at temperatures below 1°K is dependent on the absence of temperature gradients between the salt pill and the vapor pressure thermometer and between the aluminum sample and the salt pill during the respective calibrations. When the salt pill was at the same temperature as the helium bath and the mechanical switch open, the total heat input to the salt pill and sample was about 10 ergs/min, presumably from vibrations. This figure can be combined with the thermal resistance between the vapor pressure thermometer and the salt pill to yield a maximum temperature difference of less than 10^{-4} deg, which is consistent with the observation that

[10] C. G. B. Garrett, Ceremonies Langevin-Perrin (College de France, Paris, 1948).
[11] N. E. Phillips, Phys. Rev. 100, 1719 (1955).
[12] Erickson, Roberts, and Dabbs, Rev. Sci. Instr. 25, 1178 (1954).

calibration points taken with helium exchange gas after the completion of an experiment agreed with those based on the mechanical heat switch to within the experimental error of 10^{-3} deg. An upper limit to the temperature difference between the aluminum sample and salt pill during the calibration of the resistance thermometer can be otained by multiplying the total heat input to the salt pill and sample, 100 ergs/min, by the thermal resistance between them, obtained by observing the change in resistance of the thermometer produced by supplying a measured power to the heater on the sample. The upper limit obtained in this way is 0.003° at 0.15°K and 0.001° at 0.3°K.

The absence of significant temperature differences between the resistance and vapor pressure thermometers during the calibration for measurements in the liquid helium region was established in the manner outlined above for the mutual inductance—temperature calibration.

Aluminum Sample

The aluminum had a purity of 99.998%; the only impurity detectable by spectrographic methods was 0.002% of copper. The sample, a 212.64 g polycrystal with a grain size of 3–5 mm, was cast in vacuum in a high-purity graphite mold, machined to shape, and vacuum-annealed at 450°C for 48 hours. This was not the sample on which the earlier measurements[1] were reported but it was prepared from the same batch of aluminum.

The superconducting transition in zero magnetic field was largely complete within a temperature interval of 0.001° at 1.163°K, as demonstrated by recording changes in sample temperature at a constant heater power. Figure 1 shows the result of such a measurement: within 0.001° at 1.163°K there is a change of slope by a factor of 2.3. An additional indication of the sharpness of the transition is furnished by two series of heat capacity measurements covering the transition region with temperature increments of 0.002°K and 0.005°K. These are shown in Fig. 5.

Heat Capacity of Addenda

The heat capacity measurements gave the sum of the heat capacities of sample, thermometer, heater, copper foil for connection to superconducting or mechanical switch, and varnish used for thermal contact. The correction for the addenda was based on an experimental determination of their heat capacity between 1.2°K and 4.2°K and an extrapolation to lower temperatures on the assumption that the heat capacity could be represented by the sum of two terms, one linear in temperature and the other cubic, which was found to fit the measured values from 1.2°K to 3.0°K. The experimental points and the line used for the extrapolation are shown in Fig. 3.

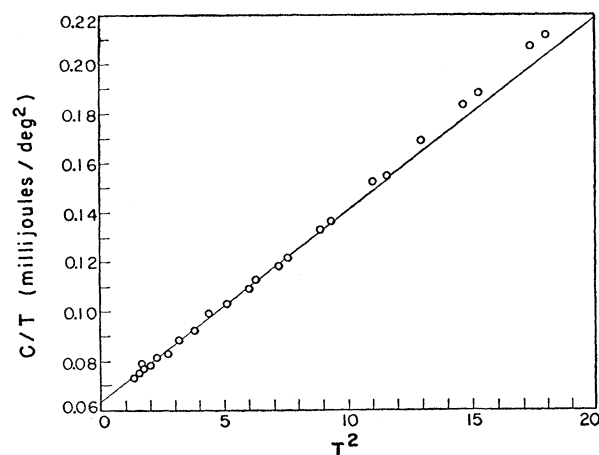In practice, the amount of General Electric 7031

FIG. 3. Heat capacity of the addenda.

varnish used was not exactly the same in different experiments and to allow for this the heat capacity of the addenda was measured twice, once with the amount of varnish normally used, and a second time with about 200 mg additional. In all cases the varnish was diluted with an equal volume of toluene and dried at room temperature.[8] The heat capacity of the varnish is given in Table I.

The magnitude of the correction for the heat capacity of the addenda was as follows: in the normal state, from 1.6% at 4.2°K to 0.6% at all temperatures below 1°K; in the superconducting state, 15% at 0.17°K, 3% at 0.3°K, and 0.2% at 1.1°K.

III. EXPERIMENTAL ERROR

For the purpose of estimating experimental errors each heat capacity point in the liquid helium region can be considered as derived from the relation $C = (Q/\Delta R)dR/dT$, in which Q is the heat input, ΔR is the change in resistance of the thermometer, and dR/dT is the temperature coefficient of the thermometer.

The value of Q involves measurement of the length of the heating period and the heater power, each of which was determined with sufficient accuracy that the error in $Q/\Delta R$ is just the error in ΔR. With temperature increments of 1/20 to 1/10 of the absolute temperature the extrapolation of the temperature drifts into the heating period amounted to only about $\frac{1}{2}\%$ of the total temperature rise and the accuracy of the measurement of ΔR was fixed by the thermometer sensitivity at about 0.1%. This figure also represents the over-all precision of the measurements.

It is known that slight differences in the experimental method employed in vapor pressure measurements can lead to differences of several millidegrees in the apparent temperature but these effects are so imperfectly understood that no correction can be applied and systematic errors of this amount must be expected. An indication of the probable size of the errors introduced into heat

capacity measurements can be obtained by comparing the two temperature scales in current use.[13] The T_{55E} and T_{55L} scales differ by as much as 0.003°, the maximum percentage difference of 0.25 occurring between 1°K and 1.5°K. Furthermore, the difference between the two scales changes by 0.006° in the interval between 2°K and 4°K with the consequence that values of dR/dT calculated on the two scales will differ from each other by an average of 0.3% in that interval. This suggests that systematic errors of a few tenths of a percent will occur both in the mean temperature and in the heat capacity.

For the measurements in the adiabatic demagnetization range the temperature drifts are greater, partly because the heat capacity is smaller, and partly because the superconducting switch has a less favorable "on-off ratio" than the mechanical switch. The precision of the measurement of $Q/\Delta R$ is about 2% for the normal state and for the superconducting state above 0.4°K but the small value of the superconducting state heat capacity at the lowest temperatures, less than 100 ergs/mole deg, makes the temperature drifts particularly great and reduces the precision. In the worst cases the extrapolation is 50% of the total temperature rise and the precision is about 20%.

Temperature measurements below 1°K are based on the magnetic temperature scale for copper potassium sulfate and in this case the heat capacity is given by $C = (Q/\Delta R)(dR/dM)(dM/dT)$, where M is the mutual-inductance bridge reading. The estimated upper limit to the temperature difference between the salt pill and the aluminum sample during the thermometer calibration would produce an error of about 2% in dR/dM and in the temperature at 0.15°K, but only a negligible error at temperatures greater than 0.3°K. If it is assumed that the salt follows a Curie-Weiss law, the accuracy of dM/dT depends on the accuracy with which the constants in Eq. (3) are measured. If Δ were known exactly, A and B would be determined by the calibration points with an accuracy such that the fractional error in the extrapolated temperatures would be comparable to that in the calibration points, about 0.1%. Actually, Δ must also be determined by the calibration points and the linearity of the M vs $(T-\Delta)^{-1}$ plot is not sensitive to small changes in Δ; furthermore, there is

TABLE I. Heat capacity of general electric 7031 varnish.

T (°K)	C/T^3 (10^{-6} joules/g deg^4)
4.0	47
3.5	46
3.0	44
2.5	41
2.0	39
1.5	39

[13] F. G. Brickwedde, *Proceedings of the Conférence de Physique des Basses Températures, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), pp. 608–610.

the possibility that an erroneous value of Δ is chosen to compensate for systematic errors in relating vapor pressure to temperature. An error of several millidegrees in Δ is therefore quite possible and this can have an appreciable effect on the calculated heat capacities and temperatures. For example, if Δ is taken as 0.028° instead of 0.033° and the constants A and B are changed so as to preserve the fit of the calibration points to Eq. (3) at 1.5°K and 4.2°K, the calculated heat capacities would be decreased by 0.6%, 3.4% and 14.5% at 1.0°K, 0.3°K, and 0.1°K, respectively, and the corresponding values of the temperature would be decreased by 0.1%, 1.0%, and 4.7%. With the new set of values for A, B, and Δ, Eq. (3) would not represent the calibration points as well but in no case would the difference be more than 0.003°.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The heat capacity measurements are in three series: 0.1°K to 0.4°K, using a tin superconducting switch; 0.3°K to 1.2°K, using a lead switch; and 1.1°K to 4.0°K, using only the mechanical heat switch. The adiabatic demagnetization region was covered in two separate experiments because the change in magnetic field necessary to operate the lead switch introduced enough energy to warm the aluminum sample to 0.3°K at the start of each heat capacity run and, although the lower critical field of tin made it possible to reach lower temperatures, the tin switch did not perform satisfactorily near 1°K. All superconducting-state measurements were made with the earth's field compensated. With the exception of three runs through the transition region, for
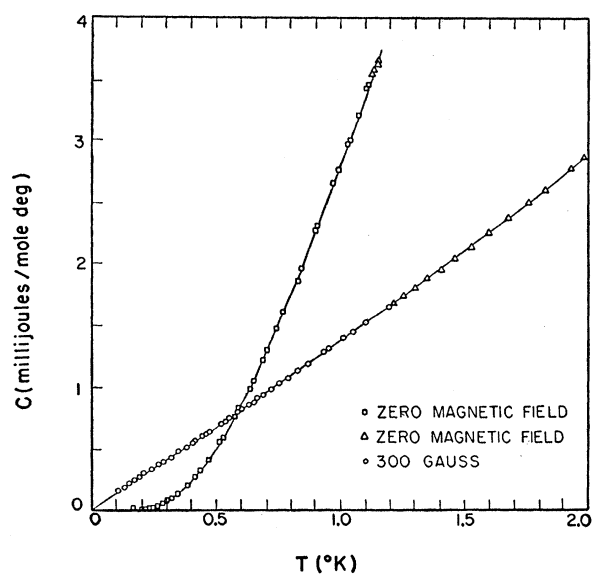

FIG. 4. Heat capacity of aluminum from 0.1 to 2.0°K. The two experiments in the adiabatic demagnetization range are designated by squares for the normal state and circles for the superconducting state. The triangles represent points taken at liquid helium temperatures.

TABLE II. Normal-state heat capacity C_n and superconducting-state head capacity C_s. Values in millijoules mole^{-1} deg^{-1}.

Measurements in liquid helium region. Temperature calculated on Leiden 1955 scale.					
T	C_n	T	C_n	T	C_n
1.2182	1.685	4.0097	6.992	3.4773	5.711
1.3017	1.808	1.1879	1.644	3.8296	6.538
1.4064	1.964	1.2565	1.745	2.7818	4.290
1.5300	2.152	1.3532	1.889	3.0774	4.689
1.6774	2.380	1.4668	2.057	3.3951	5.535
1.8286	2.620	1.6012	2.263	3.7374	6.319
1.9832	2.872	1.7632	2.515		
2.1669	3.180	1.9313	2.787	T	C_s
2.3866	3.559	2.1047	3.072		
2.6017	3.947	2.3121	3.428		
2.8060	4.333	2.5138	3.789	1.1290	3.55
3.0409	4.795	2.7040	4.142	1.1361	3.58
3.3163	5.362	2.9229	4.563	1.1513	3.63
3.6431	6.094	3.1783	5.075	1.1526	3.65

Measurements in adiabatic demagnetization region. Temperatures are based on extrapolation of the susceptibility of copper potassium sulfate.					
T	C_n	T	C_n	T	C_n
0.1185	0.174	0.2794	0.386	0.9582	1.331
0.1346	0.196	0.3040	0.422	1.0499	1.469
0.1535	0.226	0.3320	0.452	0.3082	0.426
0.1760	0.248	0.3689	0.508	0.3599	0.498
0.1976	0.281			0.4045	0.554
0.2171	0.308	0.3640	0.500	0.4565	0.622
0.2418	0.338	0.4080	0.557	0.5139	0.708
0.2688	0.374	0.4643	0.628	0.5529	0.759
0.2945	0.405	0.5334	0.725	0.5946	0.824
0.3222	0.442	0.5908	0.804	0.6357	0.872
0.3562	0.488	0.6524	0.889	0.6945	0.953
0.3875	0.530	0.3413	0.471	0.7567	1.044
0.1118	0.158	0.4164	0.574	0.8303	1.152
0.1307	0.194	0.4755	0.650	0.8697	1.211
0.1704	0.246	0.5422	0.741	0.9319	1.297
0.1863	0.267	0.6046	0.827	1.0159	1.418
0.2002	0.288	0.6668	0.923	1.1018	1.540
0.2130	0.301	0.7240	0.994	1.1924	1.653
0.2326	0.327	0.7925	1.091		
0.2576	0.356	0.8712	1.204		

Measurements in adiabatic demagnetization region. Temperatures are based on extrapolation of the susceptibility of copper potassium sulfate.					
T	C_s	T	C_s	T	C_s
0.2058	0.0109	0.3272	0.0991	0.9049	2.269
0.2323	0.0203	0.2402	0.0229	0.9736	2.660
0.2314	0.0175	0.2695	0.0402	1.0381	3.002
0.2055	0.0110	0.2953	0.0588	1.1124	3.444
0.2264	0.0162	0.3182	0.0916	0.3852	0.201
0.2017	0.0122	0.3503	0.137	0.4432	0.336
0.1887	0.0066	0.3889	0.210	0.5210	0.568
0.2239	0.0178			0.5803	0.772
0.2423	0.0230	0.4210	0.273	0.6382	0.993
0.2600	0.0313	0.4731	0.407	0.6934	1.230
0.1718	0.0087	0.5329	0.592	0.7462	1.478
0.2103	0.0133	0.5932	0.819	1.0333	2.987
0.2302	0.0167	0.6530	1.055	1.1078	3.430
0.2386	0.0201	0.7099	1.305	0.3191	0.0906
0.2284	0.0181	0.7732	1.609	0.3840	0.198
0.2514	0.0281	0.8471	1.973		
0.2693	0.0399	0.9096	2.297		
0.2891	0.0547	0.9961	2.768		
0.3054	0.0748	1.0745	3.215		
0.3126	0.0815	0.8296	1.868		

which smaller temperature rises were used, the increments were between 1/20 and 1/10 of the mean temperature. The results are collected in Table II and the points below 2°K are plotted in Fig. 4.

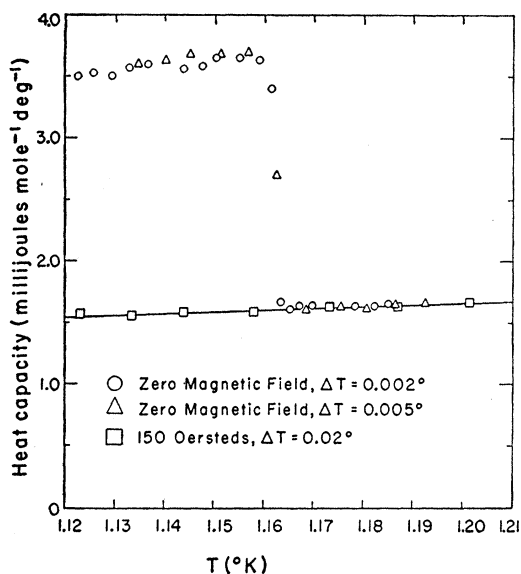The runs in which small temperature increments were employed covered an interval of 0.09°K at the transition

FIG. 5. The transition region. The different symbols distinguish three separate runs through the transition temperature, $1.163°K$.

temperature and are shown in Fig. 5. The transition in zero magnetic field was complete within a single heating period covering either 0.005° or 0.002°.

Normal-State Measurements in the Liquid Helium Region

The results of normal-state measurements at liquid helium temperatures are shown in Fig. 6 as fractional deviations from Eq. (1) with $\gamma = 1.350 \times 10^{-3}$ joules/mole deg^2 and $\theta = 427.7°$. In addition to the T_{55L} scale, which is a vapor pressure-temperature relation calculated from other thermodynamic data and which was used in Table II, the results are shown as calculated on two other scales: the T_{55E} scale[14] which is an empirical vapor pressure-temperature relation based on a variety of direct and indirect measurements; and a modified thermodynamic scale calculated by van Dijk and Durieux[15] using the results of a recent heat capacity determination on liquid helium by Hill and Lounasma.[16] With the exception of three points between 1.2 and 1.5°K, the experimental values are all within 0.1% of a smooth curve and two-thirds are within 0.05%.

Depending on the choice of temperature scale the results either fit Eq. (1) or deviate from it by as much as one-half percent; thus it is of interest to consider the degree to which the equation can be expected to approximate the heat capacity. Calculations based on a lattice

model[17,18] indicate that departure of the lattice heat capacity from the T^3 law would not be important in this case but it has been suggested by Buckingham[19] that the modification of the density of states near the Fermi level, brought about by the electron-phonon interaction, would lead to an anomaly in the electronic heat capacity of normal metals. The theory has been developed[5] only for the case of nonsuperconductors, for which the predictions cannot be tested by existing experimental data, but the possibility that the electronic heat capacity in the present case might depart from proportionality to the temperature by a few tenths of a percent seems not to be ruled out.

The three temperature scales involved differ by no more than 0.003°K, which is comparable to the apparent difference in temperature that can be produced by slightly different conditions in the vapor pressure bulb
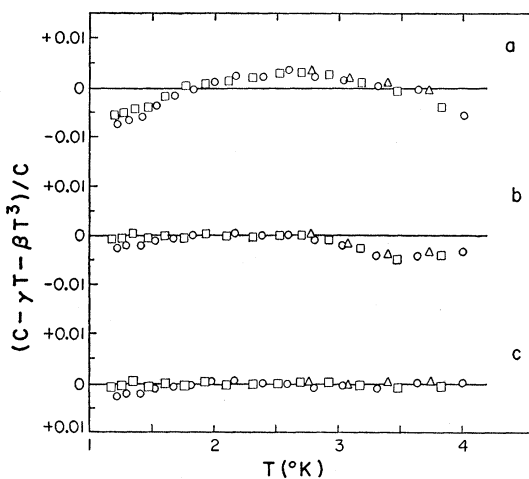

FIG. 6. Normal-state measurements at liquid helium temperatures. The results are calculated on three different temperature scales: (a) T_{55E}; (b) T_{55L}; (c) a scale similar to T_{55L} but based on Hill and Lounasma's values for the heat capacity of liquid helium.[15] $\gamma = 1.350$ millijoules/mole deg^2; $\beta = (12/5)\pi^4 R(427.7)^{-3}$. The different symbols represent three different heat capacity runs.

and tube.[20] Consequently, even if it is assumed that Eq. (1) does represent the correct temperature dependence to within 0.1%, the results cannot be considered as evidence favoring one scale over the others except for this particular apparatus. On the other hand, the results of measurements in this apparatus are reproducible; the features of Fig. 6 were duplicated by a completely separate set of measurements, not reported here, on the same aluminum sample but with a different heater, thermometer, etc. On this basis it may prove possible to reach some conclusions about the above points by

[14] Clement, Logan, and Gaffney, Phys. Rev. 100, 743 (1955).

[15] H. van Dijk and M. Durieux, Physica 24, 1 (1958). The scale used in the calculations is the one employing the value $L_0 = 59.50$ joules/mole for the latent heat of vaporization at 0°K and is the same as T_{55L} below 2.7°K.

[16] R. W. Hill and O. V. Lounasma, Phil. Mag. 2, 143 (1957).

[17] R. B. Leighton, Revs. Modern Phys. 20, 165 (1948).

[18] J. de Launay, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 289.

[19] M. J. Buckingham, Nature 168, 281 (1951).

[20] See, for example, E. Ambler and R. P. Hudson, J. Research Natl. Bur. Standards 56, 99 (1956).

comparing measurements on different metals made under identical conditions. At present it can only be deduced that the heat capacity is represented by Eq (1), within limits of error set by the temperature measurements, with $\gamma = (1.350 \pm 0.01) \times 10^{-3}$ joule/mole $\deg^2$ and $\theta = 427.7 \pm 1.0°$. These figures are compared with other values in Table III.

Values of the low-temperature elastic constants are available[21] and can be compared with the lattice heat capacity. The vibrational spectrum of the face-centered cubic lattice has been calculated by Leighton[17] using a central-force model including nearest and next-nearest neighbor interactions. Fuchs[22] has attributed the failure of the Cauchy relation for cubic metals to the necessity of modifying the central force model to include the contribution of the electron gas to the elastic constants, and de Launay[23] has estimated the consequent change in the frequency spectrum for two extreme cases:

TABLE III. Comparison of normal-state parameters with other determinations.

	γ (millijoules mole^{-1} deg^{-2})	θ (deg)
Calorimetric		
This work	1.35	427.7
Kok and Kessom[a]	1.45	419
	1.43[f]	408[f]
Howling, Mendoza, and Zimmerman[b]	1.37	375
Critical field data		
Goodman and Mendoza[c]	1.23	
Daunt and Heer[d]	1.08	
Theoretical		
de Launay[e]		426.6

[a] J. A. Kok and W. H. Keesom, Physica **4**, 835 (1937).
[b] Howling, Mendoza, and Zimmerman, Proc. Roy. Soc. (London) **A229**, 85 (1955).
[c] B. B. Goodman and E. Mendoza, Phil. Mag. **42**, 594 (1950).
[d] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 1324 (1949).
[e] See reference 18.
[f] These values were obtained by recalculation on the 1949 scale by Howling, Mendoza, and Zimmerman (see footnote b). The plot of C/T vs T^2 was not linear so the assignment of values was to a certain extent arbitrary.

Case 1, in which the electrons take no part in the thermal vibrations, and Case 2, in which they follow them. For aluminum, the calculated values of θ_0, the Debye characteristic temperature at the absolute zero, are 421.0° and 426.6°, respectively.[18] The observed value, 427.7 $\pm 1.0°$, is in agreement with de Launay's Case 2 as might be expected for the low-frequency modes which are excited at these temperatures. The measurements do not extend to sufficiently high temperatures to test the predicted temperature dependence of θ, which corresponds to only 0.15% of the total heat capacity at 4.0°K.[18]

Normal-State Measurements in the Adiabatic Demagnetization Region

In Fig. 7 the values of C/T for the normal state in the adiabatic demagnetization region are plotted against T^2

[21] P. M. Sutton, Phys. Rev. **91**, 816 (1953).
[22] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1935).
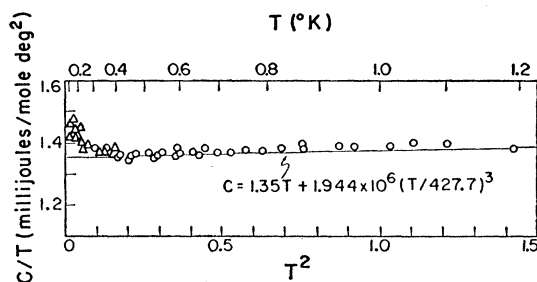[23] J. de Launay, J. Chem. Phys. **21**, 1975 (1953).

FIG. 7. Normal-state measurements in the adiabatic demagnetization region. The straight line is an extrapolation from measurements at liquid helium temperatures. The results of two completely separate experiments are distinguished by the different symbols.

and compared with an extrapolation of Eq. (1) from the liquid helium region. A smooth curve through the experimental points would be above the extrapolation by about 10% at 0.1°K, 2% at 0.3°K, and 1% for temperatures greater than 0.4°K. As discussed in Sec. III, this is just the behavior that would be expected if the value of the Weiss constant for copper potassium sulfate used in establishing the temperature scale was too high by 0.005°, an amount which cannot be considered unreasonable in view of the possible errors in vapor pressure measurements and in the helium vapor pressure-temperature relation. Within the experimental error then, Eq. (1), with the values of γ and θ determined above 1°K, represents the normal-state heat capacity to 0.1°K.
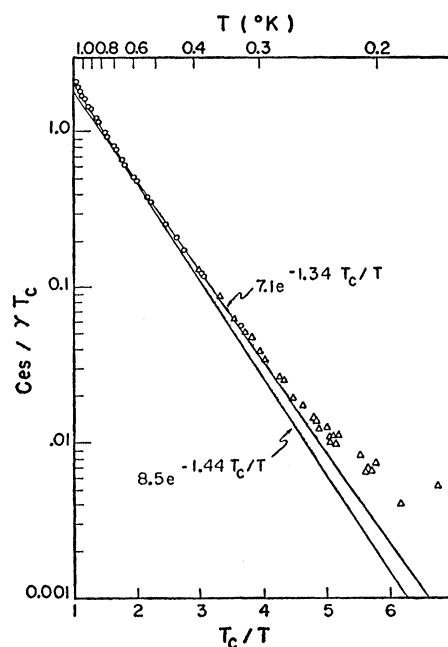

FIG. 8. Electronic heat capacity in the superconducting state, C_{es}. The different symbols distinguish the results of two completely separate experiments.
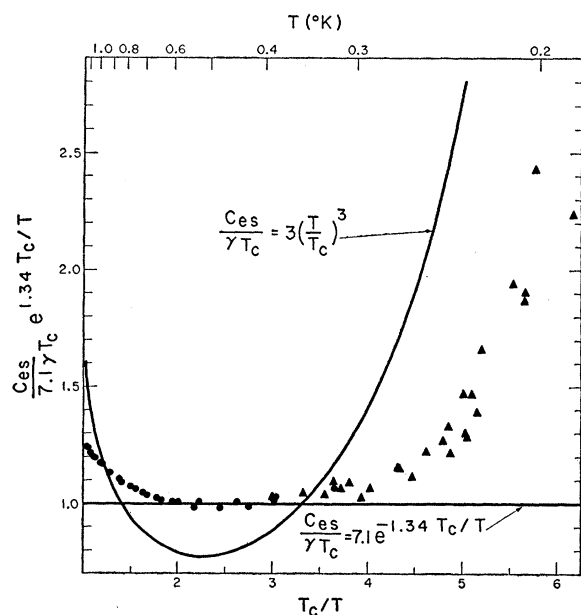
FIG. 9. Electronic heat capacity in the superconducting state, C_{es}, compared with the T^3 law and with an exponential temperature dependence. The different symbols distinguish the results of two completely separate experiments.

Superconducting State

The electronic heat capacity in the superconducting state, C_{es}, was calculated on the basis of the usual assumption that the lattice heat capacity is the same in the two states. The correction for the lattice heat capacity amounted to between 1 and 3%. In Fig. 8 the results are plotted as $\log(C_{es}/\gamma T_c)$ vs T_c/T to facilitate comparison with the exponential dependence on temperature that has been observed in other superconductors and which is a feature of the Bardeen, Cooper, and Schrieffer[7] (BCS) theory. The points do not approach a straight line at low temperatures; consequently, the assignment of values to the constants a and b of Eq. (2) is not unique, but depends on the reduced temperature range in which the fit is made. This is shown more clearly in Fig. 9. The BCS theory gives values for a and b of 8.5 and 1.44, respectively, for reduced temperatures in the range of about 0.3 to 0.5.[7] It is evident from Fig. 8 that these values would fit the experimental points only for reduced temperatures 0.5 to 0.7 and that at lower temperatures the discrepancy increases with decreasing temperature. Furthermore, the theoretical value of b approaches 1.75 in the low-temperature limit making the difference between the theoretical and experimental slopes greater than that shown. For other superconductors, at reduced temperatures between 0.3 and 0.5, values of a and b have been reported as follows: tin, 9.17 and 1.5[24]; vanadium, 9.17 and 1.5[25]; zinc, 5.8 and

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[24] W. S. Corak and C. P. Satterthwaite, Phys. Rev. **102**, 662 (1956).

[25] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956).

1.22.[26] In this same range of reduced temperatures the values of a and b for aluminum are 7.1 and 1.34, respectively. It is clear that the electronic heat capacities of different superconductors do not satisfy a law of corresponding states of the form $C_{es}/\gamma T_c = f(T/T_c)$ where f is the same function for all superconductors.

Other quantities that can be compared with predictions of the BCS theory are the discontinuity in the electronic heat capacity in zero magnetic field, $C_{es}(T_c)/\gamma T_c$, and $\gamma T_c^2/H_0^2$, in which H_0 is the critical magnetic field at 0°K. These quantities are related to the form of the energy gap at T_c and at 0°K, respectively and, according to the theory, should be the same for all superconductors. For $C_{es}(T_c)/\gamma T_c$ the observed and theoretical values are respectively 2.43 and 2.52; for $\gamma T_c^2/H_0^2$, 1.71 and 1.70. The experimental values vary from one superconductor to another and a correlation between $\gamma T_c^2/H_0^2$ and T_c/θ has recently been pointed out.[27]

The large deviation of C_{es} from a simple exponential temperature dependence at reduced temperatures below 0.2 occurs in the region in which the temperature measurements are least accurate and other sources of error greatest but it does seem to be outside the experimental error. It cannot be explained in the same way as the deviation of the normal state data from Eq. (1). The use of an incorrect value of Δ in establishing the magnetic temperature scale, or any other source of error in the thermometer calibration, would produce the same fractional error in each case but, at the temperature of the lowest superconducting state point, 0.17°K, the measured C_{es} is greater than 7.1 $\exp(-1.34\ T_c/T)$ by a factor of 4 although the measured C_n apparently exceeds that calculated from Eq. (1) by only 7%. For the observed behavior to be entirely a consequence of temperature scale inaccuracies would require an error in the thermometer calibration at 0.2°K of about 0.035° which is well outside the estimated experimental error and which seems unlikely in view of the normal state results. The possibility that the high value of C_{es} and C_n at the lowest temperatures might be due to an additive heat capacity contribution which is present in both states but not included in Eqs. (1) or (2) can be ruled out by the observation that the additional term in C_n would have to be twice the total superconducting state heat capacity at 0.17°K. Further support for these arguments comes from the results of measurements on zinc, made in the same apparatus under identical conditions. At all temperatures C_n shows the same percentage deviation from Eq. (1) as it does for aluminum but at 0.17°K C_{es} is greater than the extrapolated exponential by a factor of 2 compared to the factor of 4 for aluminum.

A possible source of error peculiar to the superconducting state measurements is the presence of "frozen-in" normal state inclusions produced as a result of the

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[26] N. E. Phillips, Phys. Rev. Letters **1**, 363 (1958).

[27] B. B. Goodman, Compt. rend. **246**, 3031 (1958).

sample becoming superconducting in a low field from the magnet or the superconducting switch solenoid instead of in zero field. To account for the observed value of C_{es} in the neighborhood of 0.2°K about 3.5% of the sample would have to be in the normal state. This seems unlikely in view of the ideal behavior of the sample in other respects but the possibility was checked by allowing the sample to become superconducting in zero magnetic field, making use of the nonzero conductivity of the superconducting switch in the open position, and taking several heat capacity points just below T_c. The presence of 3.5% of normal material would reduce the heat capacity by 2% at T_c but, within the scatter in the points of 0.3%, the results were the same as those obtained when the sample became superconducting at 0.17°K in a magnetic field and was subsequently heated to T_c.

The failure of an exponential function to express the temperature dependence of C_{es} at low reduced temperatures would argue against the existence of a constant energy gap at those temperatures. A recent and comprehensive review of the experimental evidence related to the existence and temperature dependence of an energy gap[28] shows that there is general support for a gap of the form proposed by BCS but that this support is based largely on measurements at higher reduced temperatures. In addition, the interpretation of some of the Knight-shift measurements[29] seems incompatible with a vanishing density of states at the Fermi level.

Most calorimetric data in the liquid helium region do not extend to low enough reduced temperatures to compare with the lowest temperature measurements in the present case. The work on vanadium[25] and tin[24] extending to T_c/T of 3.4 and 4.2, respectively, is within the range over which the data of Figs. 8 and 9 might be approximated by a straight line and the data for tin actually show about the same amount of curvature as do the aluminum results over their common reduced temperature range. Measurements on niobium to $T_c/T = 7$ have recently been reported[30] which show deviations from an exponential temperature dependence qualitatively similar to those in Fig. 8.
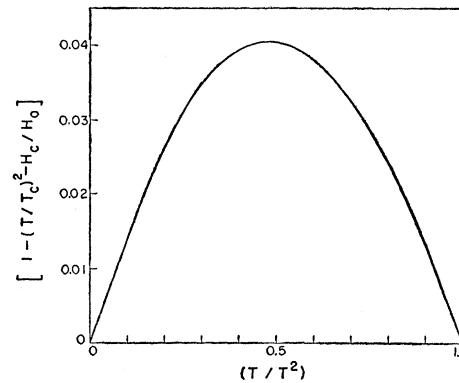
In the adiabatic demagnetization region measure-

FIG. 10. The critical field H_c shown as the deviation from the parabolic law, $H_c = H_0[1 - (T/T_c)^2]$. $H_0 = 103.0$ gauss.

ments made on zinc in the same apparatus show a deviation from the exponential similar to that for aluminum.[26] Goodman's data for aluminum[2] at temperatures below $T_c/T = 2.5$ show a less pronounced curvature on a plot of log C_{es} vs T_c/T than do the present results and could be approximated by an exponential with a smaller value of b but this would not represent the best fit in the region in which the parameters a and b have usually been evaluated. His data for vanadium give a low temperature increase in the value of b over the 1.5 observed for T_c/T between 2 and 4.[25]

Critical Field

The critical field, H_c, has been calculated from the heat capacity data and is shown in Fig. 10 as the fractional deviation from the parabolic law, $H_c = H_0 \times [1 - (T/T_c)^2]$. The maximum deviation of 4% is comparable to that found in other superconductors except mercury and lead[28] and to that predicted by the BCS theory. The calculated value of H_0 is 103.0 gauss compared with the value 106 gauss obtained by the extrapolation of magnetic measurements according to the parabolic law.[31]

[28] Biondi, Forrester, Garfunkel, and Satterthwaite, Revs. Modern Phys. 30, 1109 (1958).
[29] F. Reif, Phys. Rev. 106, 208 (1957).
[30] Chou, White, and Johnston, Phys. Rev. 109, 688 (1958).

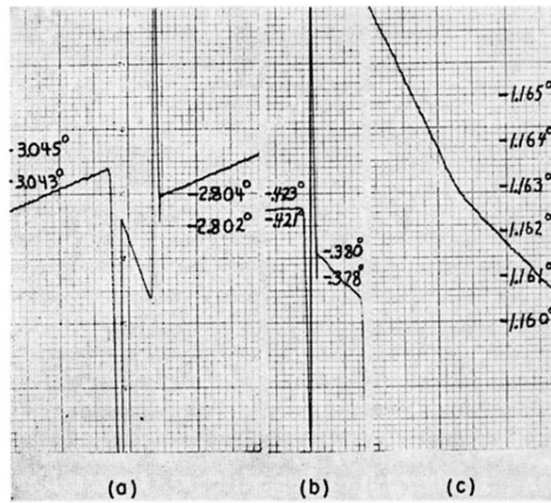[31] B. B. Goodman and E. Mendoza, Phil. Mag. 42, 594 (1950).

FIG. 2. Typical heating curves. (a) Heat capacity point in the liquid helium region. The outer abrupt changes in slope occur at the beginning and end of the heating period; the others are produced by changing the amplifier gain or potentiometer voltage. (b) Heat capacity point in the adiabatic demagnetization region. (c) Heating curve through the superconducting transition at constant power.