Superconducting and Normal Specific Heats of a Single Crystal of Niobium*

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The anomalous specific heat found in a polycrystalline sample of niobium and previously reported from this laboratory by Hirshfeld, Leupold, and Boorse (HLB) prompted complete remeasurements both in the normal and superconducting phases on a single crystal with lower tantalum content. The thermal constants of the single crystal show only small differences from the polycrystal in the same temperature range, the single-crystal values being $T_c=9.20$°K and $\Theta=241$°K between about 10° and 3°K. The normal-state single-crystal measurements agree with measurements on the HLB polycrystal made both in this laboratory and by van der Hoeven and Keesom at Purdue University. The latter measurements were carried to about 0.4°K in a field of 17 kG. As a result of their investigation, they report a Debye Θ of 275°K in the region below 3°K. With this value of Θ, the anomaly in the specific heat disappears. As both the single-crystal results and the van der Hoeven and Keesom values agree in the mutually measured ranges, Θ is taken to be 275°K. The corresponding value of γ is found to be 7.80 mJ/mole deg^2. The usual exponential behavior of the electronic specific heat $C_{es}/\gamma T_c=ae^{-bT_c/T}$ with $a=8.21$ and $b=1.52$, is observed over a restricted temperature range. Below $t=5$ the data exhibit larger values than predicted by the exponential in agreement with a number of other superconductors. The value of the energy gap at 0°K was found to be 3.69 kT_c. Overall comparisons are made with the BCS theory and a modification due to Swihart.

I. INTRODUCTION

EXTENSIVE measurements of the specific heat of niobium in the temperature interval from approximately 12 to 1.2°K have been reported previously from this laboratory.[1–3] The latest measurements made by Hirshfeld, Leupold, and Boorse[3] (HLB) on a polycrystalline specimen showed that the normal phase, obtained by the application of a magnetic field of approximately 10 000 G, had a specific heat which could be represented by the usual sum of an electronic and lattice term, viz., $C_n=\gamma T+\text{const}(T/\Theta)^3$ with $\gamma=7.53$ mJ/mole deg.[2] The data indicated that in the range 12 to about 3°K, the value of Θ was constant and equal to 238°K. At lower temperatures the specific-heat values were larger than those given by the C_n relation, but the presence of 0.2% tantalum in the sample and the very high fields[4] required to suppress completely superconductivity in Nb alloys prompted the explanation of the larger values as a consequence of the appearance of the mixed phase in the material. Accordingly, the value of Θ appropriate to the normal phase over the whole interval to absolute zero was taken as constant and equal to 238°K. Previous measurements on annealed Nb made by Chou, White, and Johnston[5] gave values varying from about 250°K near the transition temperature to approximately 320 near 2°K. The precision of the latter values was apparently much less than those at the higher temperatures. Leupold and Boorse[2] using an annealed single crystal found a constant value equal to 241°K. Further evidence for a constant value of Θ approximately equal to that found in the previous researches reported from this laboratory has been given by Morin and Maita.[6] Using a field of 18 kG, they found Θ constant and equal to 230°K from above the transition to 1.5°K.

The superconducting-phase specific heat C_s in the HLB investigation was carefully measured in a number of separate trials because it was found that with $\Theta=238$°K, C_s below 1.7°K was smaller than the lattice specific heat in the normal phase. Although a similar anomaly had previously been found in indium by Bryant and Keesom,[7] the fact that Nb is a hard superconductor and likely to show significant variation in properties from sample to sample, prompted further measurements on a better specimen. Preliminary measurements[2] on a single-crystal rod, $\frac{3}{8}$ in. in diameter, obtained from Materials Research Corporation, Orangeburg, New York, did not show the anomaly. Accordingly, careful measurements were made again on both the polycrystal and on another piece of the same single-crystal rod mentioned above. The remeasurement of the polycrystal yielded identical results within the error of measurement with the originally published values.[3] In order to improve the superconducting properties of the second piece of the single-crystal rod, it was subjected to a zone-refining process. This operation was effected through the kindness of Dr. J. E. Kunzler and E. Buehler of the Bell Telephone Laboratories, Murray Hill, New Jersey, where the specimen was subjected to four passes in an electron-beam melting apparatus in high vacuum. The specimen, as subsequently analyzed, showed that as compared to the HLB polycrystalline

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material,[3] the tantalum content was lower, being 750 parts per million as compared with 2000; N_2, 54 ppm as compared with 248; O_2 at 34 ppm, Fe at 25 ppm and Si at 75 ppm were all slightly higher. Otherwise, the analysis was the same. A series of x-ray photographs taken at intervals along the length of the specimen showed identical crystal structure.

II. APPARATUS AND PROCEDURE

The apparatus used to make the measurements on this single crystal was essentially the same as that used in the HLB investigation.[3] The principal change was the replacement of the inner He-4 bath in the cryostat with an He-3 reservoir in order to reach lower temperatures. In carrying out the investigation, additional precautions were taken to insure the reliability of the temperature measurements.

As in previous investigations, temperatures were determined by the use of resistance thermometers. To measure temperatures in the He-3 range, Allen-Bradley 0.1-W carbon composition resistors having a room temperature resistance of approximately 10 Ω were used. For the He-4 range and up to 20°K, Allen-Bradley 0.1-W resistors having an approximate room temperature resistance of 33 Ω were employed. After each run, a resistance-vapor pressure calibration of the thermometer was made so that any errors arising from cycling to nitrogen temperatures or higher were avoided. The vapor-pressure temperature conversions for He-3 were made using the 1962 scale of Roberts, Sydoriak, and Sherman,[8] for the He-4 region of the 1960 scale,[9] and for the hydrogen region the scale of Wooley, Scott, and Brickwedde.[10]

The resistance-temperature curve for the He-3 region joined smoothly to the curve for the He-4 region and in the range of overlapping temperatures gave indistinguishable values. A least-squares fit of the helium calibration date was obtained for each run with the aid of an IBM 1620 computer using the relation

$$T=\frac{B}{\ln R+K/\ln R-A}.$$

The temperatures calculated by means of this formula agreed with those determined experimentally from vapor pressure measurements to within 2 or 3 millidegrees.

For each run in which heat capacity data were taken above the helium temperature region, the thermometer was also calibrated against the vapor pressure of liquid hydrogen in the range between its normal boiling point (20.4°K) and triple point (13.957°K). The H_2 and He^4 points together were then fitted with the aid of a 1620 computer to the expression

$$\ln R=A+BT^{-1/2}+CT^{-1}.$$

The agreement between values of T calculated from this formula and those obtained by observed vapor pressures was excellent, the root-mean-square error amounting to about 6 millidegrees over both the helium and hydrogen ranges. This formula was used only in the specific heat calculation at the temperatures in the gap between the He and H_2 regions where a 6-millidegree error is only of the order of 0.1% of the measured temperature.

In the uncalibrated region between liquid helium and liquid hydrogen temperatures, it was essential that some checks be provided in order that the accuracy of the specific-heat determinations as well as that of the transition temperature could be estimated. To make such checks, gas thermometer measurements of the transition temperature of a highly purified lead wire were used. The gas thermometer measurements were made at Rutgers University through the kindness of Professor B. Serin. Two determinations of the transition temperature of the lead wire were made, yielding values of 7.210±0.005° and 7.209±0.005°K. Throughout the heat-capacity measurements, the lead wire was thermally bonded to the niobium sample and readings of the resistance thermometer on the sample determined when the lead changed from the superconducting to the normal phase or vice versa. In three separate comparisons, the reading of the resistance thermometer when placed in the $\ln R$ versus T formula above yielded the following temperatures: 7.19, 7.21, and 7.21°K. It was therefore concluded that the formula based on calibrations in the He-4 and hydrogen temperature ranged was not in error at 7.21°K by more than a few tenths percent. The adoption of 7.21°K as the lead transition

TABLE I. Smoothed values of the molar specific heat of niobium.

T (°K)	T^2 (°K)^2	C_s/T (mJ/mole deg^2)	C_n/T (mJ/mole deg^2)	T_c/T
0.0	0.00	0.000	7.80	∞
0.5	0.25	0.023	7.82	18.39
1.0	1.00	0.101	7.89	9.19
1.5	2.25	0.266	8.00	6.13
2.0	4.00	0.647	8.17	4.60
2.5	6.25	1.450	8.38	3.68
3.0	9.00	2.683	8.64	3.06
3.5	12.25	4.374	9.09	2.63
4.0	16.00	6.294	9.61	2.30
4.5	20.25	8.289	10.20	2.04
5.0	25.00	10.42	10.87	1.84
5.5	30.25	12.78	11.60	1.67
6.0	36.00	15.30	12.40	1.53
6.5	42.25	17.93	13.27	1.41
7.0	49.00	20.66	14.22	1.31
7.5	56.25	23.54	15.23	1.23
8.0	64.00	26.48	16.31	1.15
8.5	72.25	29.49	17.46	1.08
9.0	81.00	32.53	18.68	1.02

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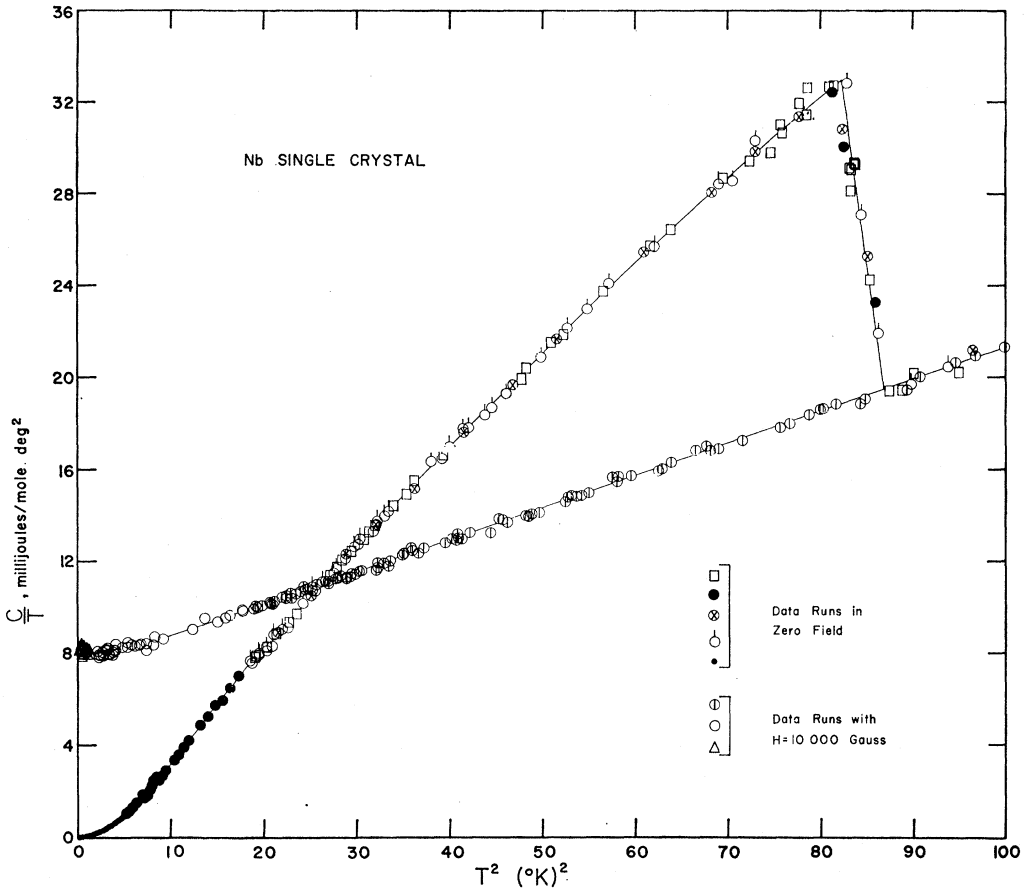

FIG. 1. C/T versus T^2 plot of the normal and superconducting specific heats of a single crystal of Nb. Full lines represent the mean values of the data.

temperature is 0.02°K higher than the latest determination[11] but more in line with the average of earlier measurements.[12]

III. RESULTS

The superconducting specific heat measured in zero field and the normal specific heat measured in a field of 10 000 G are shown in Fig. 1 and smoothed values for the data in the two phases are given in Table I. The normal data from the transition down to about 3°K can be calculated from the usual Debye-Sommerfeld relation with $\Theta=241$°K and $\gamma=7.38$ mJ/mole deg^2 obtained from the extrapolation of the $\Theta=241$°K line to 0°K in substantial agreement with the values previously reported for the polycrystal. In the present data, however, starting at T^2 values between 10 and 9, the experimental points at decreasing temperatures rise gradually above the $\Theta=241$°K normal line and fall on a new line whose Θ value was found to be 275°K with the corresponding value of γ equal to 7.80 mJ/mole deg^2. The uncertainty regarding the proper interpretation of this line suggested that the normal specific heat be determined in fields higher than the 10 000-G field available. Professor P. H. Keesom of Purdue University kindly agreed to measure the specific heat of the polycrystalline sample in a field of 17 kG in order to check the published data. The results of this investigation conducted by van der Hoeven and Keesom[13] (VK) and

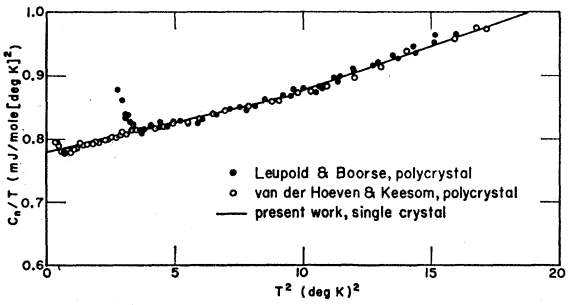

FIG. 2. C/T versus T^2 plot showing the experimental determinations of the normal specific heat below $T^2=20$. The data of van der Hoeven and Keesom is compared with polycrystal measurements in this laboratory, and the present data on a single crystal (full line) found in this investigation. The change in slope of the normal line just below $T^2=10$ should be noted.

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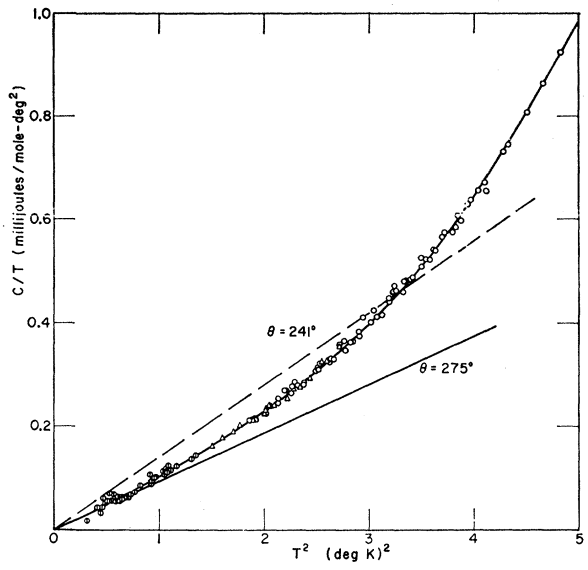

FIG. 3. C/T versus T^2 plot of the superconducting specific heat below $T^2=5$. The lines for Debye Θ values of 241° and 275° are shown for comparison.

published in this journal show clearly that the Θ = 275°K line is characteristic of the normal phase of niobium at the lowest temperatures and is not the result of the appearance of the superconducting phase.

In Fig. 2, the VK measurements are compared with those made in this laboratory on the same sample as well as with the smooth curve of the single-crystal measurements. All three sets of measurements agree within 1%. The measurements of VK show the same rise at 3° and follow the line Θ = 275 to about 0.7°K before undergoing an abrupt upward departure in the 17 000-G field. As can be seen from Fig. 2, the measurements made in this laboratory on the sample in a 10 000-G field rise sharply at about 1.8°K. This suggests that the gradual departure between $T^2=10$ and $T^2=9$ of the normal data from the line Θ = 241°K to the line Θ = 275°K reflects an inherent property of the crystal structure and not a consequence of an insufficient magnetic field as had been originally supposed. On this basis, the previously reported specific-heat anomaly disappears and the slope of the normal line corresponding to a Debye Θ of 275°K agrees with the limiting slope of the superconducting data close to the origin (see Fig. 3). It is interesting also that this value for Θ now agrees with the 277°K value found by Alers and Waldorf[14] from ultrasonic measurements at 4.2°K.

The transition temperature of the single-crystal sample was taken to be 9.19_5°K, the midpoint of the superconducting specific-heat discontinuity which extended from 9.07 to 9.32°K. A further confirmation for the view that the phonon spectrum of the metal changes in the neighborhood of 3°K is found in the experimentally determined entropy difference between the normal and superconducting phases. A plot of this difference versus temperature was found to vanish at 9.19_3°K. This value is in excellent agreement with the transition temperature taken as defined above, since the difference between 9.193° and 9.195° produces a disagreement in entropy between normal and superconducting phases of only 0.1%, less than the experimental error. If it is assumed that the change in Θ is an effect arising from imperfectly quenched superconductivity, the entropy difference vanishes at 9.13°K with the result that at 9.19_5°K the superconducting entropy exceeds the normal by about 3%. Thus an increase in Debye Θ seems to be the correct explanation for the change in slope of the normal line.

For a thermodynamically reversible superconductor, the critical field H_T at temperature T may be calculated from the relation

$$\int_T^{Tc}(S_n-S_s)dT=-(VH_T^2/8\pi). \qquad (1)$$

The entropy difference (S_n-S_s) for the single crystal was found by plotting a large scale graph of $(C_n/T-C_s/T)$ against the temperature and then measuring the appropriate areas with a planimeter. Using the values for the entropy difference thus obtained, Eq. (1) was integrated graphically and H_T could then be calculated after choosing $V=10.8$ cc/mole.[15] The resulting temperature dependence of H_T is shown on the graph in Fig. 4 and numerical values of H_T are given in Table II. The critical field H_0 at 0°K was found to

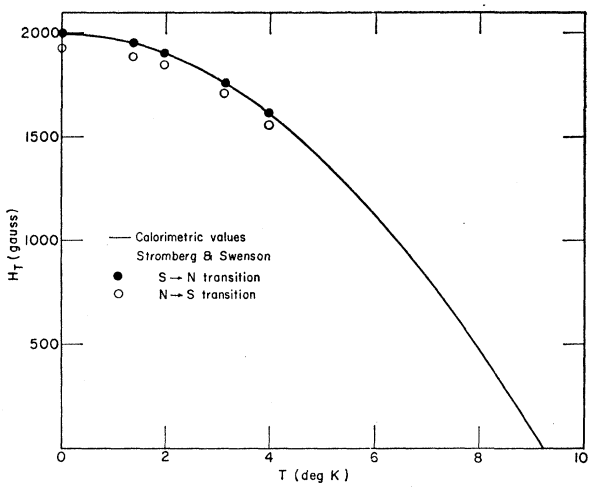

FIG. 4. Critical field versus temperature for the single-crystal specimen of Nb deduced from the specific-heat measurements, compared with critical-field measurements taken from the data of Stromberg and Swenson for transitions from normal to superconducting (open circles) and superconducting to normal (dots). The agreement of the latter data with the critical field deduced from these specific-heat measurements is obvious.

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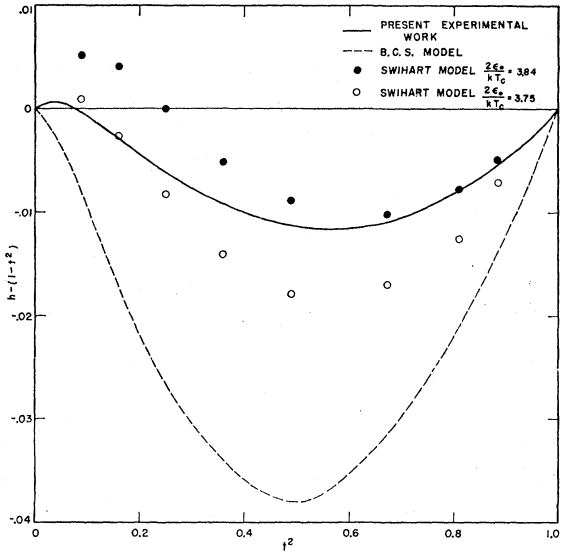

FIG. 5. Deviation of the critical field of the single-crystal Nb specimen determined from the specific-heat measurements from the parabolic dependence (full line). Dashed curve is the deviation according to the BCS theory. Open circles and dots are for comparison with Swihart's calculations.

be 1994 G. This is in excellent agreement with the field deduced from calorimetric measurements by McConville and Serin[16] who found the value 1990 G. The value deduced from direct magnetic measurements by Stromberg and Swenson[17] was 1960±40 G. The critical-field values of the latter investigation were obtained by taking the average of values measured when going from the superconducting to the normal phase and when going in the reverse direction. It is interesting to note that their superconducting to normal values of the critical field agree with those determined calorimetrically in the present work to within one-half of one percent. (See Fig. 4.)

TABLE II. Critical fields and deviation from parabolic law.

T	$t=T/T_c$	H_T	$h=H_T/H_0$	t^2	$h-(1-t^2)$
0.0	0.0000	1994	1.0000	0.0000	0.0000
0.5	0.0544	1988	0.9972	0.0030	+0.0002
1.0	0.1088	1971	0.9986	0.0118	+0.0004
1.5	0.1632	1942	0.9770	0.0266	+0.0006
2.0	0.2176	1901	0.9532	0.0473	+0.0005
2.5	0.2720	1847	0.9262	0.0740	+0.0001
3.0	0.3263	1780	0.8926	0.1065	−0.0009
3.5	0.3807	1700	0.8527	0.1450	−0.0023
4.0	0.4351	1608	0.8067	0.1893	−0.0040
4.5	0.4895	1501	0.7546	0.2396	−0.0058
5.0	0.5439	1389	0.6966	0.2958	−0.0076
5.5	0.5983	1262	0.6329	0.3579	−0.0092
6.0	0.6527	1124	0.5635	0.4260	−0.0105
6.5	0.7071	974.3	0.4887	0.4999	−0.0114
7.0	0.7615	814.8	0.4086	0.5798	−0.0116
7.5	0.8158	644.6	0.3233	0.6656	−0.0111
8.0	0.8702	465.1	0.2333	0.7573	−0.0095
8.5	0.9426	275.6	0.1382	0.8549	−0.0069
9.0	0.9790	78.19	0.0392	0.9585	−0.0023

If the deviations of the reduced critical fields from a parabolic relation are plotted against the square of the reduced temperature, the curve is unusual because it has both positive and negative values. The only other superconductor in which comparable behavior has been observed is indium. The niobium curve is also atypical in that its maximum negative deviation is only about one-third that of most other superconductors and of that required by the BCS theory.

Following Goodman,[18] the value of the energy gap $2\epsilon_0$ at 0°K can be estimated from the relation:

$$2\epsilon_0/kT_c=(\tfrac{4}{3})\pi(H_0^2V/8\pi\gamma T_c^2)^{1/2}.$$

Using the single-crystal values of γ, H_0, T_c found in this investigation, $2\epsilon_0/kT_c=3.69$, compared with the value 3.52 required by the BCS theory.

The value obtained from ultrasonic measurements by Dobbs and Perez[19] depends on the propagation direction in the crystal; being 3.77 for the [100] direction, 3.74 for the [111], and 3.65 for the [110]. Levy, Kagiwada, and Rudnick,[20] using transverse waves, found 3.7 and 3.5, depending on the method of analysis. The value found from the tunneling experiments of Giaever[21] was 3.6, from Sherril and Edwards[22] 3.59, and from Townsend and Sutton[23] 3.84±0.06. A value of 3.8±0.2 has been found by Mendelssohn[24] from thermal conductivity measurements. The present value lies in the range of these determinations.

The BCS theory predicts an electronic specific heat at the transition C_{es} equal to $2.43\gamma T_c$. The value found for $C_{es}/\gamma T_c$ in these measurements is 2.87.

If the electronic specific heat C_{es} is calculated in the usual way, viz:

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

using $\gamma=7.80$ mJ/mole deg^2, the plot of $\ln C_{es}/\gamma T_c$ versus T_c/T gives a straight line for values $5.5>T_c/T>1.7$, indicative of the relation

$$C_{es}/\gamma T_c=ae^{-bT_c/T}.$$

This is shown in Fig. 6. The data obtained from this plot yields $a=8.21$ and $b=1.52$ in fair agreement with the predicted BCS values of 8.5 and 1.44. At values of

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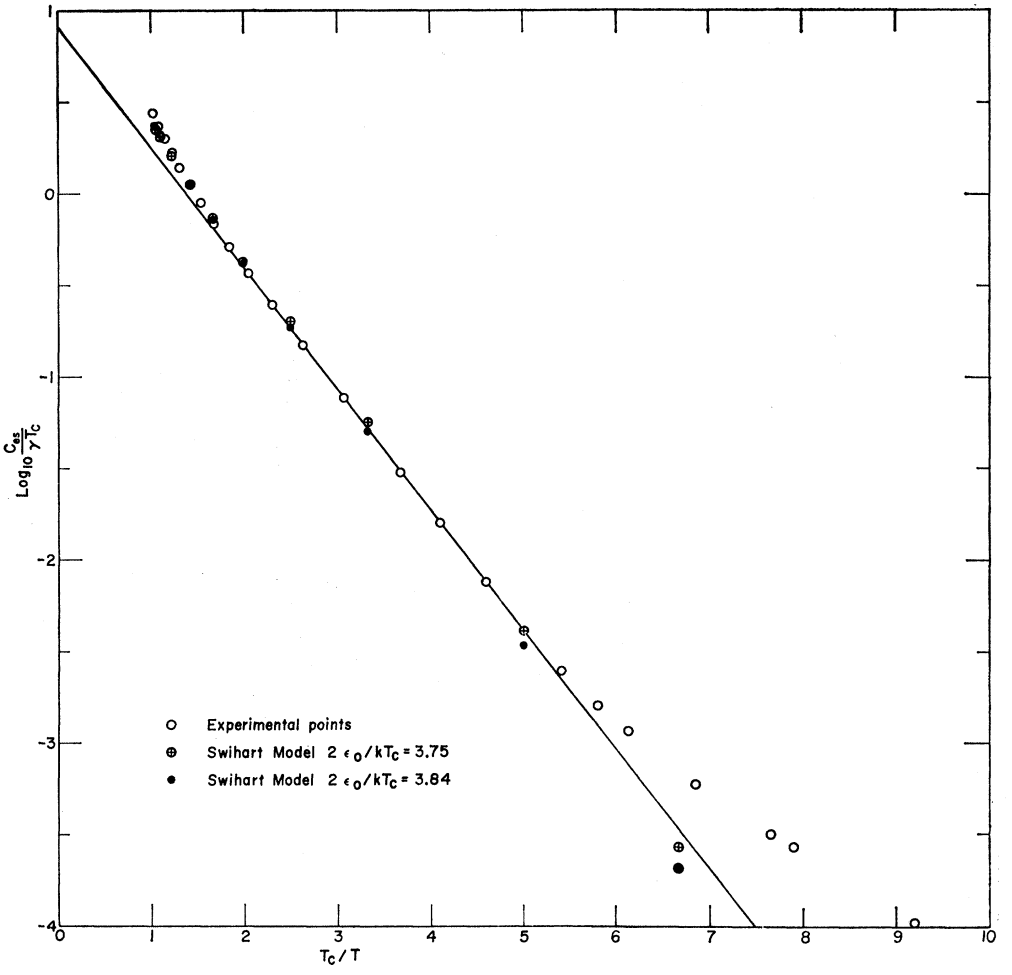

FIG. 6. The superconducting electronic specific heat C_{es} of a single-crystal specimen of Nb plotted on $\ln_{10}(C_{es}/\gamma T_c)$ versus T_c/T axes. Full line is the graph of $C_{es}/\gamma T_c = ae^{-bT_c/T}$, where $a=8.21$ and $b=1.52$. The dots and crossed circles show values computed from Swihart's model.

$T_c/T>5.5$ the data departs from the exponential as will be discussed below.

Although the BCS theory gives fair agreement with the a and b values, the critical-field deviation curve, the value of the energy gap and the specific-heat jump at the transition all show significant disagreement. However, the BCS calculations were made under the assumption of weak coupling, i.e., that T_c/Θ is small, of the order of 0.003 or less, as for elements such as Zn, Al, and Ga. When T_c/Θ is an order of magnitude greater, however, as is the case for Nb (0.033 for $\Theta=275°K$ and 0.039 for $\Theta=241°K$) and In (0.039), the energy gap value increases to about 3.7 and the critical-field deviation has a minimum only about one-third to one-half as low. (See Fig. 5.) Moreover, the deviation actually is positive at the lowest temperatures as was mentioned above. For elements with still higher values of T_c/Θ, e.g., Hg (0.056) and Pb (0.075), the deviation becomes positive throughout the entire temperature range from 0°K to the transition temperature.

Calculations of these properties of superconductors which give closer agreement with the experimental data have been supplied by Swihart in a private communication. He assumed that the energy gap $\epsilon(T)/\epsilon(0)$ was the BCS function of reduced temperature and remained constant with energy out to a cut off of $13.7\epsilon(0)$ instead of to infinity as used in the weak-coupling case by BCS. The calculations were made for two cases, one assuming the ultrasonic energy gap $2\epsilon(0)/kT_c=3.75$ and the other the value 3.84 obtained from tunneling. These cases correspond to values of T_c/Θ of 0.039 and 0.038, respectively, which are much closer to the values 0.033 and 0.038 for niobium than the weak-coupling values to which the BCS procedure is applicable.

The electronic specific heats calculated by Swihart are compared to the experimental values in Fig. 6. The values are seen to be relatively intensitive to the assumed energy gap values and both sets of calculations agree well with the experimental data for $T_c/T<5.5$. In contrast to the specific-heat curve of BCS which is applicable only from inverse reduced temperatures greater than about 2.0, the Swihart model agrees well with experiment with T_c/T values almost to the transition temperature. For values of T_c/T greater than 5 or 6, both the BCS theory and Swihart's modification predict a downward displacement of $C_{es}/\gamma T_c$ from the

exponential. As can be seen from Fig. 6, however, the experimental points show an upward displacement at higher inverse reduced temperatures. A similar upward departure has been observed in several other superconductors[25,26] and is generally believed to be due to anisotropy of the energy gap. Although this rise in specific heat is greater than the probable experimental error, the electronic component, C_{es}, is very small at these temperatures and approaches the order of magnitude of the scatter in the data. For this reason, no accurate quantitative comparison with the ultrasonically measured anisotropy is practicable.

Swihart's calculated critical field deviations are shown together with the experimental curve in Fig. 5. The experimental curve lies between the two calculated curves except at the low temperatures where the calculated positive deviations exceed those observed experimentally. Qualitative agreement is good as the calculations show the required change in sign, and as can be seen from the graph, the quantitative results are much closer to the experimental values than are those of the BCS theory.

For $(C_{es}/\gamma T_c)_{T_c}$ Swihart's calculations yield 2.89 for an energy gap of 3.84 and 2.76 for a gap of 3.75. Again, agreement of these values with the experimental result of 2.87 is better than the predicted BCS value of 2.43.

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