

FIG. 12. Linewidth against temperature for YIG(2% Tm) with the field along [100]. Sparse data on the other principal directions indicate that the curves are very much the same. Frequency, 9.2 kMc/sec.

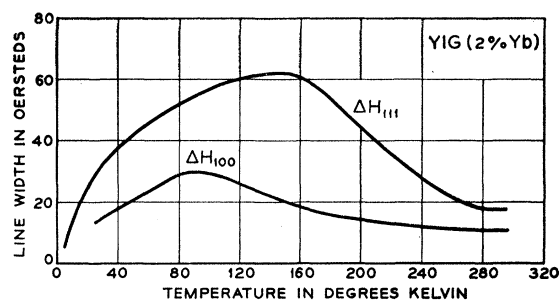


FIG. 13. Linewidth against temperature for the steady field along [111] and [100] directions in YIG(2% Yb). Frequency, 20.8 kMc/sec.

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Superconducting and Normal Specific Heats of Niobium*

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The measurements reported in this paper were undertaken to resolve differences in the published values of the low-temperature heat capacity of niobium and to determine the effect of high-temperature annealing (2340°C) and degassing on the same sample for which data had previously been published by Brown, Zemansky and Boorse. The new measurements cover the temperature interval 1.1 to 11.5°K and are significantly different from those obtained prior to the thermal treatment. The normal-phase heat capacity may be expressed by the usual relation, $C_n = \gamma T + \text{const}(T/\Theta_D)^3$, with $\gamma = (7.53 \pm 2\%)$ mJ/mole deg² and $\Theta_D = 238^\circ\text{K} \pm 1.5\%$. The zero-field transition temperature, determined from the midpoint of the transition interval, was found to be 9.09°K . In the superconducting phase below 1.7°K , the total heat capacity C_s was found to be less than the lattice specific heat alone in the normal phase. This anomalous result, previously reported by the present authors, is comparable to that found in indium by Bryant and Keesom. This anomaly complicates the determination of the superconducting electronic specific heat C_{es} but by using a theory by Ferrell, it may be evaluated in the usual form, $a\gamma T_c \exp(-bT_c/T)$, with $a = 12.6$ and $b = 1.71$.

I. INTRODUCTION

SHORTLY after publication of the Bardeen-Cooper-Schrieffer theory (BCS) of superconductivity,¹ it appeared that a useful check on the theory could be made by comparing its predictions with experimental measurements of the superconducting electronic specific heat, C_{es} , as a function of the temperature. Although a number of C_{es} measurements had been made on pure metals at reduced temperatures t between 1 and 0.25, relatively few had been reported for smaller values of t and of these, only vanadium showed the dependence required by the theory.² Niobium, being identical in crystal structure and similar in chemical properties to vanadium, appeared suitable for a further test of the

theory, especially since values of t approaching 0.1 could be obtained with liquid He⁴ and the temperatures measured with good accuracy. The disadvantage of this choice lay principally in the difficulty of securing a specimen of the requisite purity and in carrying out a heat treatment which would eliminate internal stresses, particularly those arising from interstitial oxygen and nitrogen. In this connection, Wexler and Corak³ had shown that in vanadium an increase in the amount of these gaseous inclusions decreased the transition temperature, increased the mechanical hardness, and produced in the material the irreversible characteristics of hard superconductors. Chou, White, and Johnston⁴ observed changes of the same kind in niobium; annealing at successively higher temperatures, which presumably decreased the gas in their specimen, raised the transition temperature and improved the agreement between magnetic and calorimetric measurements. How large these effects may be has been demonstrated by the

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¹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

² H. A. Boorse, *Phys. Rev. Letters* **2**, 391 (1959).

³ A. Wexler and W. S. Corak, *Phys. Rev.* **85**, 85 (1952).

⁴ C. Chou, D. White, and H. L. Johnston, *Phys. Rev.* **109**, 788 (1958).

recent investigations of De Sorbo and Nichols⁵ who find that the addition of 1.4 at. % of interstitial oxygen reduces the transition temperature of Nb from 9.465 to 5.840°K.

The specimen⁶ previously used in this laboratory to determine the heat capacity of niobium over a smaller temperature range, seemed suitable from the standpoint of purity of specimens then available but a comparison between critical magnetic fields deduced from the earlier heat capacity measurements made in this laboratory and those measured directly by Jackson and Preston-Thomas⁷ suggested that the interstitial gases had not been sufficiently reduced in the previous heat treatment. Through the kindness of Dr. Milan W. Fiske of the General Electric Company, the sample was given a further heat treatment at the G. E. Research Laboratory. The initial treatment was a slow heating in high vacuum to a temperature of 2350°C where it was maintained for one hour, following which it was cooled to 500°C in 2 h and then to room temperature in a period of about 12 h.

At the conclusion of the measurements presented in this paper, a gas and spectrographic analysis of the metal was made by the National Research Corporation, Cambridge, Massachusetts. The analysis showed that the elements Al, B, Cr, Co, Ni, Mo, Pb, Sn, and V were not present in detectable amounts; other elements were present in parts per million (ppm) as follows: Mn < 1, Mg < 5, Fe < 10, and Si = 30. As would be expected, the largest metallic impurity was tantalum, which was estimated to be about 0.2%. Test for oxygen showed 28.2 ppm while a Kjeldahl nitrogen analysis gave 248 ppm. Although the latter appears undesirably high, the detailed results presented in Sec. III of this paper nevertheless show clearly the relatively large specific heat changes produced by the high-temperature heat treatment. The chief interest attaches to the measurements at temperatures below about 1.7°K; here it was found that the total superconducting specific heat was less than the normal-phase lattice specific heat, calculated according to present ideas, at the same temperature. This result is similar to that found in indium by Bryant and Keesom.⁸ A preliminary report of the anomaly has been published by the present authors elsewhere.⁹ The purpose of this paper is to present the complete specific heat measurements of which the anomaly is a part and to exhibit the changes in specific heat which were produced by the heat treatment of the sample.

II. EXPERIMENTAL ARRANGEMENT AND PROCEDURE

The niobium sample described in the introduction above was a cylinder 0.5-in. in diameter, 1.88-in. long, having a mass of 50.50 g (0.55 mole). It was supplied by the Fansteel Metallurgical Corporation. After annealing, the first measurements were made in a cryostat described in detail elsewhere.^{6,10} An electromagnet, giving a field at the specimen of over 10 000 G, was used to obtain the normal state measurements. These measurements, hereafter referred to as the 1958 data, extend down to 1.5°K.

In order to extend the range of measurements to lower temperatures a new cryostat was built using two He⁴ bath spaces. Essential details are drawn schematically in Fig. 1. The inner liquid helium bath *B* was subject to heat conduction only from the outer liquid helium bath *A*, from which it was isolated by the vacuum space *D* and inconel pump tubes of about 6.5-in. in length. Suitable traps insured that the *B* bath received radiation only from surfaces below 4°K. In addition, special care was taken to isolate the cryostat as much as possible from the vibrations of the mechanical pumps. A 1-mm constriction *K* in the *B*-space pump tube served to reduce the perimeter available for superfluid film flow.

An Inconel tube *F* (0.125-in. i.d.) beginning just above the constriction led to a McLeod gauge which measured the vapor pressure of the *B* bath. A 0.1 W Allen-Bradley resistor *H* at the bottom of this bath served as a convenient monitor of the helium temperature. The lowest temperature reached was 0.91°K, and

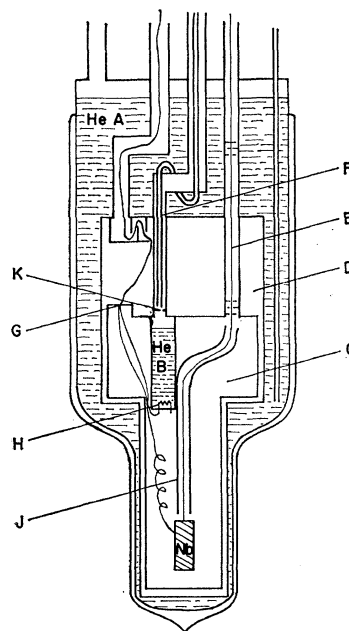


FIG. 1. Schematic cross section of the cryostat.

⁵ W. De Sorbo and G. E. Nichols, *Bull. Am. Phys. Soc.* **6**, 267 (1961).

⁶ A. Brown, M. W. Zemansky, and H. A. Boorse, *Phys. Rev.* **92**, 52 (1953).

⁷ L. C. Jackson and H. Preston-Thomas, *Phil. Mag.* **41**, 1284 (1950).

⁸ C. A. Bryant and P. H. Keesom, *Phys. Rev.* **123**, 491 (1961).

⁹ H. A. Boorse, A. T. Hirshfeld, and H. Leupold, *Phys. Rev. Letters* **5**, 246 (1960).

¹⁰ R. D. Worley, M. W. Zemansky, and H. A. Boorse, *Phys. Rev.* **99**, 447 (1955).

a full charge of 12 cc of liquid was sufficient to last for 11 h.

The sample was suspended by a nylon monofilament E attached to a winch located at the top of the cryostat, the axle being brought through the vacuum wall by a Veeco quick-coupling seal. The filament was thermally bonded to the A and B baths to reduce heat leak. By turning the winch, the sample could be pulled up against the copper tube J soldered to the B bath, and thus in good thermal contact with it. This arrangement eliminated the use of He exchange gas at temperatures below 4.2°K. Measuring circuits for the heater and thermometer were similar to those used previously in this laboratory.⁶ The resistance of the heater itself was determined as a function of the temperature, and with the specimen in the normal state, as a function of the impressed magnetic field as well.

Sample temperatures were determined from the measured resistance of an Allen-Bradley 1-W carbon resistor mounted in a hole bored transverse to the specimen axis at the midsection. At the end of each run the carbon thermometer was calibrated against the vapor pressure of helium in the A and B baths. Vapor pressures were converted to temperatures using the L_{55} scale,¹¹ and corrections were made above the λ point for the hydrostatic pressure head of the A bath, and at the lowest pressures for thermomolecular pressure effects.¹² No dependence of the thermometer resistance on magnetic field was observed. A least-squares fit of the thermometer calibration data for each run was obtained with the aid of an IBM 650 computer, using the relation $\log R + K/\log R = A + B/T$. For each run in which heat capacity data were taken above the helium region, the thermometer was also calibrated against the vapor pressure of hydrogen¹³ in the range between the normal boiling point and the triple point.

The procedure for establishing the thermometer calibration above the helium region was as follows. Using the constants A , B , and K obtained by the least-squares fit in the helium region below 4.2°K, the T , R relation was rewritten as $T' = B(\log R + K/\log R - A)^{-1}$. For several known temperatures in the helium range between 4.2°K and about 4.8°K, and in the hydrogen range between the normal boiling point and the triple

point, measured values of R were found. These values of R were then inserted in the above equation and the corresponding values of T' computed. Such values were found to be uniformly smaller than the actual temperatures determined from vapor pressure measurements. These differences between the actual and computed temperatures $\Delta \equiv (T - T')$ were found to be a simple function of $(T' - 4.2)$, expressible as $\Delta = \beta(T' - 4.2)^n$. The agreement between interpolated values of T computed in this way and those checked by observed vapor pressures was excellent, differences being uniformly small and of the order of a few tenths of a percent. Despite this excellent agreement, some check on the accuracy of the thermometer in the uncalibrated gap was necessary. For this purpose the transition temperature of pure lead, 7.17°K,¹⁴ was taken as a fixed point, and to determine the corresponding carbon thermometer resistance, a 4-mil lead wire, 99.999% pure, about 2-in. long was placed in thermal contact with the sample but insulated from it electrically. A measuring current of approximately 4 mA was set up in the wire and the potential difference across it observed continually together with values of the resistance thermometer at known times. By noting the instant at which the resistive transition appeared, the corresponding thermometer resistance could be determined and hence the transition temperature computed. Two determinations of the lead point made during the 1958 measurements gave 7.16°K; two other measurements obtained during the 1960 runs yielded values of 7.09° and 7.12°K, definitely low, but within 1% of the assumed value. The wires used in the 1958 and 1960 measurements were not the same and it is possible that the 1960 wire contained some impurities as a result of the drawing process. Such impurities would probably tend to depress the transition temperature¹⁵ and would thus account for the lower values observed.

The molar heat capacity was calculated with the aid of the IBM 650 computer from the usual relation $C = i^2 R_h t / N \delta T$, where the current i flows through the sample heater of resistance R_h , for a time t . N is the number of moles in the sample and δT is the temperature change produced by the current. Each of these quantities, with the exception of δT , was measured with an accuracy of better than 0.1%. The quantity δT was obtained from the change in resistance of the thermometer during the heating interval as discussed in a previous paper from this laboratory.⁶ The error in determining δT is greatest for superconducting data at the lowest temperatures, where the heat capacity of the sample is smallest. Here, errors in δT could be as large as 7%, although for the final run (Fig. 3—open circles) this figure was about 3%. Points above $T = 2^\circ\text{K}$, for which δT was in doubt by more than 2%, were rejected.

¹¹ H. van Dijk and M. Durieux, *Physica* **24**, 1 (1958). At the time the measurements were begun the T_{L55} scale was the latest one available in a convenient form. Comparison of T_{L55} with T_{58} [F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, *J. Research Natl. Bur. Standards* **64A**, 1 (1960)] shows a maximum difference, $\Delta \equiv (T_{L55} - T_{58})$ at a given vapor pressure in the region of calibration, of 3.2 millidegrees at 3.9°K. More significantly, $d\Delta/dT$ is greatest (1.2%) in the neighborhood of 4.2°, indicating that heat capacity determinations using the two scales for calibration would differ by that amount at 4.2°. However, use of the resistance thermometer as a secondary thermometer probably served to smooth out some of the errors in the T_{L55} scale so that any error due to improper vapor pressure scale is not as great as 1%.

¹² T. R. Roberts and S. G. Sydorak, *Phys. Rev.* **102**, 304 (1956).

¹³ H. W. Woolley, R. B. Scott, and F. G. Brickwedde, *J. Research Natl. Bur. Standards* **41**, 379 (1948).

¹⁴ W. B. Pearson and I. M. Templeton, *Phys. Rev.* **109**, 1094 (1958).

¹⁵ G. Chanin, E. A. Lynton, and B. Serin, *Phys. Rev.* **114**, 719 (1959).

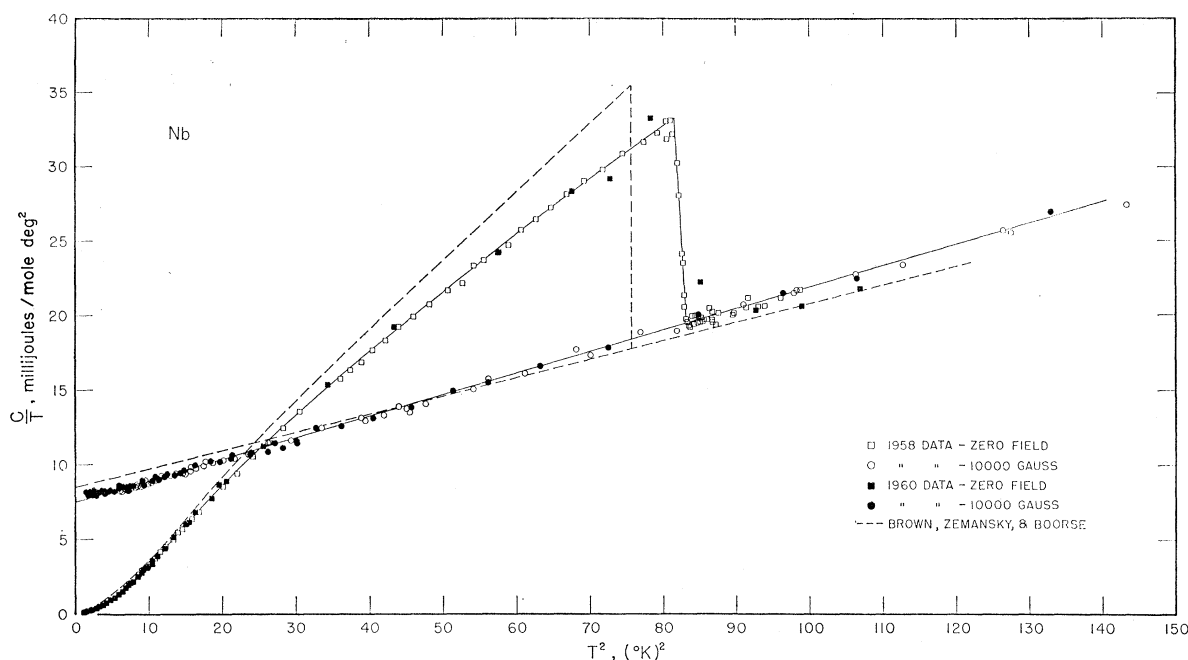


FIG. 2. C/T vs T^2 plot of the normal and superconducting specific heat of a polycrystalline sample of Nb. Full lines represent the mean of two series of measurements; blank and black squares represent data taken in zero field; blank and black circles represent data taken in a field of over 10 000 G. The dashed line represents the results of the earlier measurements of Brown, Zemansky, and Boorse on the same sample before the 2350°C heat treatment.

The heat capacity of the carbon resistor and of the glyptal on the sample made significant contributions to the measured specific heat and each had therefore to be known. Accordingly, an Allen-Bradley resistor (total mass 0.365 g of which 0.240 g was in the copper connectors) similar in size and room-temperature resistance to the one used in the niobium sample was wound with Constantan heater wire of approximately 1000- Ω resistance (mass about 3 mg). Heat capacity measurements were then made, using the resistor itself for temperature readings. The results gave $C = (0.005T + 0.0026T^3)$ mJ/deg with an estimated accuracy of 10% or 1% of the niobium heat capacity except for the superconducting data at the lowest temperatures. The mass of the glyptal during the various runs was between 0.13 and 0.16 g. Published values of this heat capacity^{16,17} which are accurate to about 20% were used to make the corrections. The glyptal correction amounted to about 3% over most of the temperature range. A reasonable estimate of the accuracy in the niobium heat capacities would be: 5% of the superconducting values at the lowest temperatures; 1% at 4°; and 1.5% at 9°. For the normal data in the same regions the figures would be 1%, 1%, and 2%. For purposes of comparison between the heat capacities in the normal and superconducting phases, the data are more reliable than the above figures indicate since the heat capacity of the addenda contributes equally to the two phases.

III. RESULTS AND DISCUSSION

The results in zero field and in a field of 10 000 G are shown in Fig. 2, in which C/T is plotted against T^2 . Smoothed values of the data for the normal and superconducting phases are given in Table I. The data taken in the magnetic field yield a linear relationship between C/T and T^2 except at the lowest temperatures ($T^2 < 3$). The solid line in Fig. 2 above $T^2 = 3$ represents a least-squares fit of the 1960 normal data to the expression $C/T = a + bT^2$, with $a = 7.53$ mJ/mole deg² and $b = 0.144$ mJ/mole deg⁴. Using these values for the normal heat capacity, a plot was made of C/T vs T and the areas between the normal and superconducting curves measured with a planimeter. They were found to agree to better than 1%, in accordance with the requirement that the entropy difference between the two phases must vanish at T_c for a second-order phase change. (It is therefore assumed that the points below $T^2 = 3$ represent the appearance of a small amount of intermediate-phase material even in a field of 10 000 G.) The fit of the lowest temperature points was not significantly improved by using an expression of the form $C/T = a + bT^2 + cT^4$.

The dashed curves in Fig. 2 show the earlier results of Brown, Zemansky, and Boorse on the same sample. The effect of heat treating the sample in preparation for these measurements is clearly evident. The transition temperature was raised in agreement with previous observations on heat treated niobium^{4,7} and tantalum¹⁸

¹⁶ N. Pearlman and P. H. Keesom, Phys. Rev. **88**, 398 (1952).

¹⁷ P. H. Keesom and G. Seidel, Phys. Rev. **113**, 33 (1959).

¹⁸ R. T. Webber, Phys. Rev. **72**, 1241 (1947).

samples, changing in this instance from 8.70 to 9.09°K. The latter figure represents the temperature at the midpoint of the transition which starts at 9.01°K and is completed at 9.17°K. The results of other workers indicate that the increase in T_c is due to the removal of absorbed gases which are present in the metal interstitially and cause straining of the lattice as noted in the Introduction. On the other hand, ordinary cold work seems to raise the transition temperature of niobium and vanadium, as is indeed true of most superconductors.¹⁹ Thus, Minnigerode²⁰ studied the effect of cold working at helium temperatures on foils of various superconductors and found an increase in T_c for niobium, from 9.4° to 9.6°K. This probably accounts for the initial decrease in T_c , from 9.668° to 9.465°K, seen by De Sorbo and Nichols on first annealing their specimen of niobium wire. A similar effect was seen by Worley *et al.*¹⁰ in vanadium. Annealing of their sample V-II led to a depression of T_c , from 4.99° to 4.89°K. A decrease would be expected since the subsequent analysis showed no change in gaseous impurities between V-II and the annealed specimen V-IIA.

The observed temperature variation of the normal heat capacity agrees with the Debye-Sommerfeld relation for normal metals at low temperatures, C_n (mJ/mole deg) = $\gamma T + 144 \times 10^3 T^3 / \Theta^3$, where the first term represents the contribution of the free electrons and the second term that of the lattice vibrations. As a result of the heat treatment the value of γ changed from 8.54 to 7.53 mJ/mole deg² and the Debye Θ from 252 to 238°K. This is in agreement with the vanadium results of Worley *et al.*, if it is assumed that the differences in results for V-I and V-II in their case are due to differences in gas content of the two samples. They point out that the change in Debye Θ is in the direction to be expected from simple Debye theory since the Debye Θ is proportional to the velocity of sound, which is greater in the harder sample of higher gas content. They also observed a change in γ in the same direction as the present sample, but considerably smaller in magnitude. Chou, White, and Johnston⁴ measured the heat capacity of niobium after several anneals at successively higher temperatures. Unfortunately, they reported no normal data for their Nb I sample below 5°K and the precision of their data did not permit them to quote separate values of γ and Θ for each state of anneal. They detected no change in the superconducting heat capacity due to successive anneals.

It is generally assumed that the lattice heat capacity is identical in the normal and superconducting phases so that one can subtract the T^3 term observed in the normal phase from the total measured superconducting heat capacity C_s to find the heat capacity of the electrons

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)	C_{latt}/T (mJ/ mole deg ²)	T_c/T
1.0	1.00	0.116	7.67	0.144	9.09
1.5	2.25	0.273	7.85	0.324	6.06
2.0	4.00	0.672	8.10	0.575	4.55
2.5	6.25	1.48	8.42	0.899	3.64
3.0	9.00	2.80	8.82	1.294	3.03
3.5	12.25	4.50	9.29	1.762	2.60
4.0	16.00	6.54	9.83	2.301	2.27
4.5	20.25	8.73	10.44	2.912	2.02
5.0	25.00	11.05	11.12	3.595	1.82
5.5	30.25	13.48	11.88	4.350	1.65
6.0	36.00	15.90	12.70	5.177	1.51
6.5	42.25	18.50	13.60	6.076	1.40
7.0	49.00	21.15	14.57	7.046	1.30
7.5	56.25	24.00	15.61	8.089	1.21
8.0	64.00	27.00	16.73	9.203	1.14
8.5	72.25	30.00	17.92	10.39	1.07
9.0	81.00	33.10	19.17	11.65	1.01

in the superconducting phase, C_{es} . This assumption applied to the present data leads to the results shown in Fig. 3. Here the superconducting measurements are exhibited in greater detail for the region below $T^2=5$. The solid line represents the molar lattice heat capacity calculated from the normal data. The total molar heat capacity in the superconducting state below $T^2=3$, is less than that for the lattice alone. A similar result was found in indium below $T^2=0.6$ ($T_c/T=4.4$) by Bryant and Keesom.⁸ Chou, White, and Johnston⁴ apparently had an indication of this same effect in their niobium measurements, for in calculating the superconducting electronic specific heat from the relation $C_{es}=C_s - C_n + \gamma T$ they state that "The choice of γ is important if a positive value for C_{es} at the lowest temperatures is to be obtained." For this reason, they chose $\gamma=19.0 \times 10^{-4}$ cal mole⁻¹ deg⁻², even though their measurements yielded a value of $(18.0 \pm 1.0) \times 10^{-4}$ cal mole⁻¹ deg⁻². ($=7.52 \pm 0.42$ mJ mole⁻¹ deg⁻²).

A straight line (not shown) drawn through the mean of the low-temperature points below $T^2<2$ in Fig. 3 extrapolates to absolute zero. At these temperatures the electronic contribution is negligible so that an obvious interpretation would be to assume that the Debye Θ is different in the normal and superconducting phases; the value in the superconducting phase, as determined from the slope of this line, being 257°. Neutron scattering experiments by Wilkinson *et al.*²¹ show no detectable change in the scattered intensity above and below the transition temperature such as one would expect from a change in the Debye Θ . However, the minimum change in Debye Θ necessary to account for our results, about 8%, may have been undetectable within the limits of error of their experiment. Wilkinson *et al.* were looking for a decrease in Debye Θ and state that "a

¹⁹ However all available data on Ta [W. Meissner, K. Steiner, and P. Grassman, Z. Physik. **36**, 519 (1935); and W. T. Ziegler, W. F. Brucksch and W. Hickman, Phys. Rev. **62**, 354 (1942)] shows a depression of T_c with cold work.

²⁰ G. von Minnigerode, Z. Physik **154**, 442 (1959).

²¹ M. K. Wilkinson, C. G. Shull, L. D. Roberts, and S. Bernstein, Phys. Rev. **97**, 889 (1955).

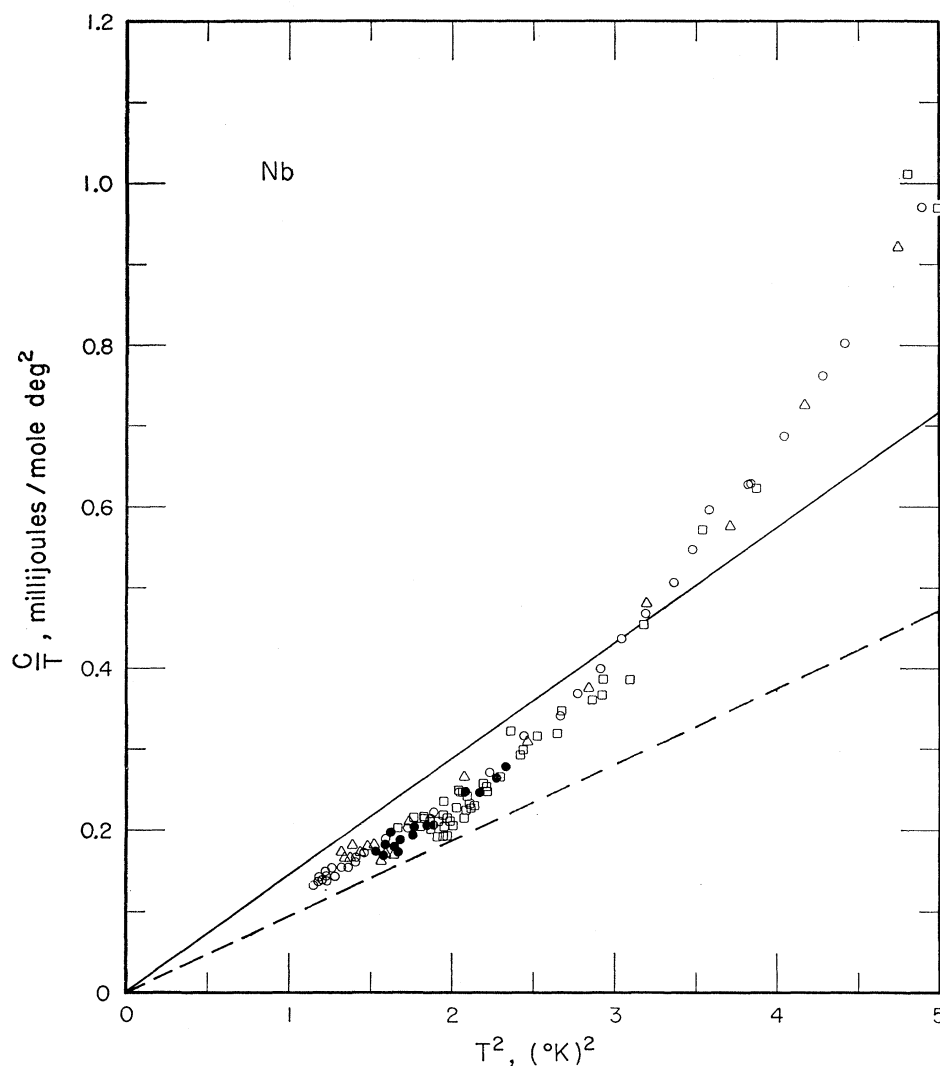


FIG. 3. C/T vs T^2 plot of the superconducting specific heat of Nb for the temperature interval $0 < T < 2.24^\circ$. Triangles, circles, squares, and dots represent the data obtained in four separate measurements. The full line represents the lattice specific heat alone as determined from normal-phase measurements with $\Theta_D = 238^\circ\text{K}$. The broken line represents the lattice specific heat for $\Theta_D = 277^\circ\text{K}$ as determined from elastic moduli measurements.

decrease in the characteristic temperature for the superconducting state of 20° would be about twice the probable error of the measurements." It appears from their Fig. 3 that an *increase* in Debye Θ of 20° would be more consistent with their findings. More recently Alers and Waldorf²² have measured the changes in the elastic moduli of niobium associated with the superconducting transition using 10-Mc sound pulses. From their data they calculate a decrease in the Debye Θ in the superconducting state of 0.016°K which is less than a 0.1% change. Neutron spectrometer measurements by Woods and Brockhouse²³ of the change in lattice vibration frequencies in lead in going from the normal to the superconducting phase also show a change, if any, of less than 0.2%. The actual value of the Debye Θ obtained by Alers and Waldorf from their measurements

at 4.2°K , is 277°K (corresponding to the dashed line in Fig. 3), in disagreement with the value of 238°K obtained in this investigation. A similar discrepancy has been observed in vanadium²⁴ where the value obtained from the elastic measurements, 399.3°K , is much larger than the largest low-temperature calorimetric value of $338^\circ \pm 5^\circ\text{K}$.²⁵ The higher figure seems to be in somewhat better agreement with the phonon spectrum of vanadium measured by incoherent neutron scattering.²⁶ To explain this difference Alers²⁴ has suggested that the measured calorimetric value of Θ may be the sum of two T^3 terms, one arising from lattice vibrations and a second smaller contribution of unknown origin which also varies as T^3 . If this explanation holds for niobium, then the true lattice term would be represented by a

²² G. A. Alers and D. L. Waldorf, Phys. Rev. Letters **6**, 677 (1961).

²³ A. D. B. Woods and B. N. Brockhouse, Bull. Am. Phys. Soc. **7**, 63 (1962).

²⁴ G. A. Alers, Phys. Rev. **119**, 1532 (1960).

²⁵ W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **102**, 656 (1956).

²⁶ C. M. Eisenhauer, I. Pelah, D. J. Hughes, and H. Palevsky, Phys. Rev. **109**, 1046 (1958).

Debye Θ of 277°K and assuming this value also in the superconducting phase, one obtains the dashed lattice line *below* the data shown in Fig. 3. This indicates that the electronic specific heat is now too large because the observed total superconducting specific heat at the lowest temperatures should be indistinguishable from the normal lattice line. Furthermore such a suggestion cannot apply to the indium data where the observed calorimetric value, $\Theta=108^\circ\text{K}$, is in good agreement with the value of 111.3°K, obtained from the elastic constants.²⁷

Recently Ferrell²⁸ has proposed an explanation of the observed anomalies in indium and niobium, in terms of an anomalous dispersion in the phonon spectrum of the superconducting phase. According to his view the phonon frequencies are changed by virtual excitations of electron-hole pairs. However, in the superconducting phase, the existence of the gap in the electron energy spectrum means that there is a region in which these excitations do not take place. Therefore the phonon spectrum in the superconducting phase is shifted upward in frequency relative to the normal state. At a given temperature fewer of the high-frequency oscillations are excited in the superconducting phase, and this leads to a lattice specific heat, smaller than in the normal phase, and given by: $C_{ls}=\alpha T^3-BT^2$, where α is the coefficient of the lattice specific heat in the normal phase. It is not possible to predict from existing data which elements will show a lattice specific heat anomaly.

If the data represented by the open circles of Fig. 3 are replotted as C_s/T^2 vs T as suggested by Ferrell, the agreement with a straight line parallel to the lattice line ($\Theta=238^\circ\text{K}$) is quite good, giving an intercept $T_s=0.25^\circ\text{K}$. This procedure assumes, of course, that in this region the electronic contribution is negligible.

Writing the superconducting heat capacity C_s as $C_s=C_{ls}+C_{es}$, and making use of Ferrell's expression for C_{ls} , the temperature variation of the electronic term, C_{es} , can be calculated. However, as a result of the presence of the new adjustable parameter B and the scatter in the lowest temperature data, the accuracy of the comparison of C_{es} with the prediction of the BCS theory is reduced. Nevertheless a plot of $C_{es}/\gamma T_c$ given in Fig. 4 shows that this quantity follows the approximate relation deduced from the BCS theory, $C_{es}/\gamma T_c=a$

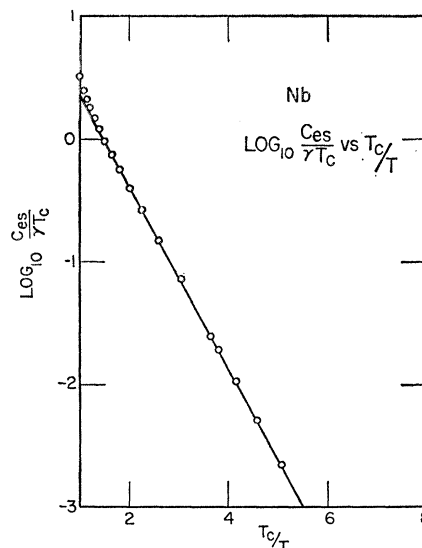


FIG. 4. The superconducting electronic specific heat C_{es} of polycrystalline Nb plotted on $\log_{10}(C_{es}/\gamma T_c)$ vs T_c/T axes. Owing to the anomaly shown in Fig. 3, C_{es} is calculated on the assumption that the superconducting lattice specific heat $C_{ls}=\alpha T^3-BT^2$ as suggested by Ferrell.

$\exp[-bT_c/T]$ with $a=12.6$ and $b=1.71$. These values may be compared with $a=10$ and $b=1.63$ which were reported⁹ for this sample after the 1958 measurements and before the low-temperature superconducting specific heat measurements reported in this paper were made.

Recently, single-crystal samples of Nb have been obtained by this laboratory and a new series of measurements are currently under way for comparison with the present results, especially those at the lowest temperatures reported in this investigation.

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²⁷ B. S. Chandrasekhar and J. A. Rayne, Phys. Rev. Letters **6**, 3 (1961).

²⁸ R. A. Ferrell, Phys. Rev. Letters **6**, 541 (1961).