PHYSICAL REVIEW VOLUME 134, NUMBER 5A 1 JUNE 1964

Specific Heat of Niobium between 0.4 and 4.2°K*

B. J. C. VAN DER HOEVEN, JR., AND P. H. KEESOM
Purdue University, Lafayette, Indiana
(Received 26 December 1963)

Below 3.3°K, the normal-state specific heat of niobium, measured in a magnetic field of 17 kG, can be represented by $C_n = 7.79T + 0.094T^3$ mJ/mole deg. This corresponds to a value of the Debye parameter at 0°K, $\Theta(0)$, of 275°K. The specific heat in the superconducting state does not appear to be anomalous, as has been reported.

INTRODUCTION

THEORY predicts that the lattice specific heat of a superconductor should be the same in both the normal and superconducting states. The normal-state specific heat is a sum of an electronic term γT and the lattice term C_{ln}. Since for sufficiently low temperatures the superconducting electronic contribution C_{es} becomes negligible, the total superconducting-state specific heat C_s is equal to the lattice contribution C_{ls}. So, for reduced temperatures above $T_c/T = 5$ one expects $C_s = C_{ln}$.

Two independent measurements of indium have provided an exception to this rule, however.[1,2] The superconducting specific heat C_s was found to be 10–20% less than the normal lattice contribution C_{ln}. A similar anomaly was reported by Hirshfeld *et al.* for niobium.[3] Recent conversations with Dr. Boorse have encouraged independent measurements and he was kind enough to offer one of his samples. The results are reported below.

EXPERIMENT

The apparatus was the He^3 cryostat described previously.[4] A germanium thermometer, similar in composition to the one described in an earlier publication[5] was used. Resistance range of the thermometer was 40Ω at 4.2°K, 120Ω at 1.0°K, and 500Ω at 0.4°K. The thermometer was calibrated in separate runs at zero field and at 17 kG. Magnetoresistance of the thermometer, $\Delta\rho/\rho$, varied from minus 2% at 4.2°K to plus 8% at 0.4°K. The 1962-He^3 temperature scale of Sydoriak and Roberts[6] for the range 0.4 to 1.2°K was used in conjunction with a paramagnetic salt thermometer for values below 0.5°K for the zero-field measurements and the 1958-He^4 temperature scale[7] above 1.0°K. An expansion of $1/T$ in powers of $\ln R$ up to $(\ln R)^3$ was done on an IBM-7090 digital computer, using the method of least squares as described by Moody and Rhodes.[8]

Total correction for the addenda (thermometer, heater, and glyptal) was less than 10% of the total heat capacity of the sample in the superconducting state at the lowest temperature. As the heat capacity of the addenda is known within ±3%, this introduces an error of at most 0.3% in the specific heat. Use was made of the most recent data of Ho *et al.*[9] for the constantan heater wire.

Normal-state measurements were made with a new set of cans incorporating the use of a superconducting Nb_3Zr wire solenoid with an inner diameter of 2.5 cm. The working volume was 1.5 cm in diameter and 3.5 cm long. A field of 17 kG was applied. In the superconducting state, a Helmholtz coil arrangement was employed to cancel the earth's magnetic field. The cylindrical sample of 0.365 moles was the same one used by Hirshfeld *et al.* with a small piece cut from the bottom. Dimensions were 1.3 cm in diameter, and

TABLE I. Specific heat of niobium. (C is in mJ/mole deg.)

T (°K)	C_s	T (°K)	C_n
0.372	0.038	0.568	4.52
0.723	0.077	0.647	5.12
0.799	0.089	0.736	5.76
0.849	0.097	0.824	6.42
0.906	0.107	0.946	7.39
1.016	0.128	1.011	7.94
1.152	0.156	1.186	9.39
1.272	0.242	1.281	10.2
1.361	0.297	1.370	10.9
1.499	0.406	1.519	12.2
1.635	0.562	1.646	13.2
1.794	0.822	1.771	14.3
1.988	1.28	2.016	16.5
2.221	2.14	2.225	18.4
2.456	3.40	2.451	20.4
2.676	5.01	2.734	23.2
2.998	8.18	3.011	25.9
3.260	11.4	3.311	29.2
3.562	16.1	3.616	33.0
3.784	20.0	3.752	34.8
4.014	25.2	3.995	38.3
4.304	32.6	4.298	42.8

* Work supported by U. S. Army Research Office.
[1] C. A. Bryant and P. H. Keesom, Phys. Rev. **123**, 491 (1961).
[2] H. R. O'Neal, Ph.D. thesis, University of California, UCRL-10426, 1963 (unpublished.)
[3] A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. **127**, 1501 (1962).
[4] G. M. Seidel and P. H. Keesom, Rev. Sci. Instr. **29**, 606 (1958).
[5] B. J. C. van der Hoeven, Jr. and P. H. Keesom, Phys. Rev. **130**, 1318 (1963).
[6] S. G. Sydoriak, T. R. Roberts, and R. H. Sherman, in Eighth International Congress on Low Temperature Physics, London, 1962, p. 297 (unpublished).
[7] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **64A**, 1 (1960).
[8] D. E. Moody and P. Rhodes, Cryogenics **3**, 77 (1963).
[9] J. C. Ho, H. R. O'Neal, and N. E. Phillips, Rev. Sci. Instr. **34**, 782 (1963).

length 3.5 cm. The estimated experimental accuracy is ±2%.

RESULTS

The results for the superconducting and normal states are listed in Table I. They are also plotted in the form C/T versus T^2 in Fig. 1, together with a few points from the smoothed curve of the data of Hirshfeld *et al.* The two measurements are in very good agreement within combined experimental error. Up to 3.3°K the normal state data may be represented by

$$C_n = 7.79T + 0.094T^3 \text{ mJ/mole deg.}$$

The coefficient of the T^3 term α corresponds to a Debye parameter at 0°K, Θ(0), equal to 275°K.

In Fig. 2 is plotted an expanded portion of C_s/T versus T^2 up to $T^2=4$. If one plots here the values of

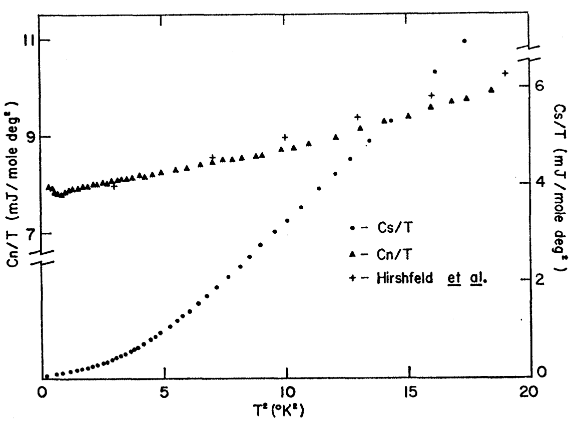

FIG. 1. C_s/T and C_n/T versus T^2.

C_s/T found by Hirshfeld *et al.*, no difference is observed. Two slopes are drawn representing the Θ(0) value of these measurements and the same quantity given by Hirshfeld *et al.* of 238°K. The small positive intercept of C_s/T (0.022 mJ/mole deg^2) will be discussed later. It is clear from this graph that the anomaly disappears using the new value of Θ(0) = 275°K.

The data for $C_{es}/\gamma T_c$ can be very well represented by $a\cdot\exp(-bT_c/T)$. Plotting in this manner yields values of $a=8.31$ and $b=1.53$, very close to those predicted by the BCS theory of $a=8.5$ and $b=1.44$.

DISCUSSION

The lattice specific heat of a metal may be expressed as

$$C_l = 1944(T/\Theta(T))^3 \text{ J/mole deg},$$

where the Debye parameter is a function of tempera-

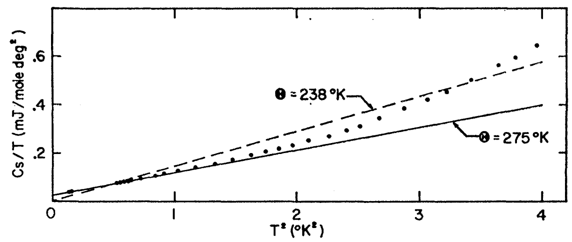

FIG. 2. C_s/T versus T^2.

ture. As mentioned before, the agreement between the values for the specific heat as measured by Hirshfeld *et al.* and these measurements are in excellent agreement within experimental error. However, the additional points at lower temperatures and with higher magnetic field modify the interpretation of the results. The initial value of Θ is now 275°K, in excellent agreement with the value derived from velocity of sound measurements by Alers and Waldorf of 277°K.[10] At 3.3°K, the value of the Debye parameter gradually decreases to a value of 238°K above 4.5°K, indicating the presence of a T^5 or higher term in the specific heat.

The increase of the normal-state specific heat at the lowest temperature may be a latent heat contribution due to insufficient quenching of the superconductivity. However, the magnitude of this deviation is within our experimental accuracy and could be due to inaccuracies in the thermometer calibration curve.

In Fig. 2 one observes that the specific heat points C_s/T gradually become tangent to the slope corresponding to Θ = 275°K at 1°K. The points do not fall below this line. Thus, the condition that $C_s = C_{ln}$ is met and no anomaly is observed.

The positive intercept of this curve with the C_s/T axis of 0.022 mJ/mole deg^2 indicates a small contribution of normal electrons. Comparing this to the value of γ in the normal state, one deduces that 0.3% of the niobium was normal. This effect may be attributed to strains or impurities. Trapping of the earth's magnetic field would make a contribution an order of magnitude too small. However, the lattice specific heat should not be influenced by this small contribution.

In conclusion it appears unnecessary to assume that the specific heat of superconducting niobium is anomalous.

ACKNOWLEDGMENT

The authors are indebted to Dr. Boorse who put his sample at their disposal.

[10] G. A. Alers and D. L. Waldorf, Phys. Rev. Letters 6, 677 (1961).