PHYSICAL REVIEW VOLUME 138, NUMBER 6A 14 JUNE 1965

Thermodynamic Properties of Molybdenum in Its Superconducting and Normal State*

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(Received 21 January 1965)

We have carried out specific-heat measurements on four samples of molybdenum in the normal and superconducting states between 0.4 and 4°K. For one sample, a detailed investigation was also made of the specific heat, the latent heat, and the critical-field curve in the region of the normal transition point T_c and in fields up to 5 G. For a reversible transition, these quantities are related by thermodynamic equations and they were found to be consistent within experimental error. The transition temperatures in zero field were found to be 0.915, 0.917, 0.918, and 0.83°K, respectively. No lambda anomaly in the specific heat could be detected there. From the measurements between 0.4 and 0.9°K, the electronic specific heat in the superconducting state was derived and compared to that expected from the BCS theory. The deviations from the theory at the low-temperature end are thought to be due to anisotropy in the energy gap. The energy-gap parameter and the critical-field curve were also deduced and compared with results from acoustic measurements.

I. INTRODUCTION

RECENTLY, very pure molybdenum was found to become superconducting at temperatures of about 0.92°K[1,2] and it seemed of interest to carry out an experimental investigation of its thermodynamic properties. Such research would indicate, for example, whether or not the superconducting transition in molybdenum is truly reversible. Also, since specific-heat measurements provide information about the energy gap in a superconductor, such a study would be useful in helping to understand the mechanism for superconductivity in the transition elements. Molybdenum appears to be an especially interesting case, since its transition temperature is extremely sensitive to small quantities of impurities, particularly magnetic ones.[1] Since very pure molybdenum samples are available now, they may show the characteristics of a "clean" superconductor.[3]

As will be described in this paper, specific heat measurements were carried out on four high-purity samples of molybdenum over the temperature range from 0.4 to 4°K. Measurements on four samples of different origin seemed essential in view of the possible effect of small impurities on the thermodynamic properties, including the electronic specific heat in the normal state. Also, for one of the samples, a high-resolution temperature-measurement technique was used to examine the superconducting transition in greater detail. High-resolution measurements of the specific heat, latent heat, and critical-field curve were carried out in magnetic fields over the range from 0 to 5 G, with particular attention being given to the width, shape and reversibility of the transition. These results will be compared to one another by means of thermodynamic relations, as has been done for other superconductors.[4,5] They will also be compared to the expected results from the BCS theory.[6]

II. EXPERIMENTAL

A. The Cryostat

The cryostat was essentially the same one as previously described[5] and liquid-He^3 or -He^4 baths were used for the temperature ranges of, respectively, 0.3 to 2°K and 2 to 4.2°K. The vapor pressure, however, was measured from a separate compartment in the helium pot. The He^3-gas-handling system was of the same type as that used by Keesom and Seidel.[7] The samples were attached by 1-mil copper ribbons to a supporting cap on which a manganin heater had been bifilarly wound. For Mo—1 and Mo—2 the supporting cap was made of thin copper, while for the heavier samples Mo—3 and Mo—4, a somewhat sturdier support was required and a quartz disc was used in place of the copper cap. The copper or quartz support cap was hung from a nylon thread by means of which the entire assembly could be drawn up tight against three indium-tipped copper prongs protruding from the bottom of the He^3 refrigerator pot. This arrangement provided a simple and effective heat switch, since the sample could be isolated thermally merely by lowering it away from the refrigerator pot.

Helmholtz coils placed outside the cryostat were used to cancel the earth's magnetic field in the region of the sample to better than 0.003 G, as determined by an air-driven flip coil. Two solenoids could be alter-

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* Work supported by a contract with the U. S. Army Research Office, Durham and a contract with the U. S. Office of Naval Research.

† Alfred P. Sloan Fellow.

[1] T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Phys. Rev. Letters **8**, 313 (1962).

[2] B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. **35**, 1 (1963).

[3] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[4] D. E. Mapother, IBM J. Res. Develop. **6**, 77 (1962).

[5] D. C. Rorer, H. Meyer, and R. C. Richardson, Z. Naturforsch. **18a**, 130 (1963).

[6] J. Bardeen, L. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957); J. Bardeen and J. R. Schrieffer, *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1961), Vol. III.

[7] G. Seidel and P. H. Keesom, Rev. Sci. Instr. **29**, 606 (1958).

nately placed around the tail of the Dewar to provide a known magnetic field for the samples. One solenoid was long and very uniformly wound and was used to apply small magnetic fields for the high resolution measurements of the critical field curve[5]; the other solenoid was used to apply a field of 180 gauss for the measurements of the specific heat in the normal state below 0.9°K.

B. Thermometry

An Allen Bradley $\frac{1}{10}$-W 30-Ω carbon resistor was used as a thermometer in the range from 4.2°K down to 0.8°K, where its resistance varied from about 300 to 60 000 Ω. This resistor was chosen for its large value of dR/dT in the temperature region near T_c for molybdenum, which provided the maximum temperature resolution obtainable with the ac bridge and phase-sensitive detector system, and thus permitted the study of the superconducting transition in great detail. Sensitivity of the ac bridge and phase-sensitive detector system was such that with a power input of 10^{-2} ergs/sec, a change of 1 Ω in 50 000 Ω could be detected. This corresponded to a temperature resolution of 5 μdeg at 0.9°K. Below 0.8°K a Speer $\frac{1}{2}$-W 470-Ω resistor was used; its resistance varied from about 2000 to 6000 Ω at 0.3°K. Actual power input to the thermometers used in the experiment ranged from 0.03 ergs/sec at the lowest temperatures up to 1.3 ergs/sec at 4°K for low-resolution measurements. The voltage input to the bridge was kept constant during any particular run, with the result that power dissipated in the thermometers was smallest at lowest temperatures, where the resistance was the greatest. For every run these resistors were calibrated against the vapor pressure of liquid helium in the refrigerator pot, using He^4 (T_{58} scale) for temperatures above 2°K and He^3 (T_{62} scale) below 2°K. Below 0.6°K, where corrections due to thermomolecular effects become appreciable, the carbon resistors were calibrated by means of the susceptibility of a spherical crystal of chromium methylammonium sulphate[8] and of an ellipsoidal sample of cerium magnesium nitrate crystals. This calibration was done in a separate experiment, where the sample was removed from the cryostat and the mutual inductance coil and the paramagnetic salt substituted in its place. Such a separate calibration was permissible because it was found that there was virtually no change in the temperature calibration of the carbon resistors from one series of measurements to the other. At the same time, while the carbon resistors were being calibrated, the relation between the observed vapor pressure versus the magnetic temperature was obtained at temperatures below 0.6°K. This calibration was in agreement with that calculated when thermomolecular corrections had been taken into account.

Using an IBM 7072 digital computer, the calibrations of T versus R for both resistance thermometers were fitted to analytical expressions by using a least-squares fit procedure. For the Allen-Bradley resistor, an expression of the form

$$1/T=a_0+a_1Z+a_2Z^2+a_3Z^3+a_4Z^{-1}+a_5Z^{-2}+a_6Z^{-3} \quad (1)$$

was used, where $Z=\ln(R-R_0)$. A Fibonacci minimization procedure was used to find the best value of R_0 for a minimum scatter of the data about the computed curve. For the Speer resistor, we used the same polynomial in Z, except that in this case $Z=R-R_0$. After obtaining these expressions and calculating the specific heat for a 99.99% copper sample, we found that a plot of C/T versus T^2 showed some small systematic deviations, of the order of 1–2% from the expected straight line. It was found that slight adjustments in the analytical expressions for the calibration curve were sufficient to correct these deviations in the specific heat curves. These corrections to the calibration were judged to be so small as still to be within the experimental error of the original calibration data. Using the C/T versus T^2 plots as a guide, the calibration was extrapolated from 0.6°K down to 0.375°K. The smoothed, extrapolated calibration expression was found to agree within experimental error with that obtained from susceptibility results. We obtained for our copper sample

$$C=(0.720\pm0.008)T+(0.0486\pm0.001)T^3, \quad (2)$$

expressed in mJ/mole°K. Both constants are in good agreements with recently compiled data[9] although the electronic term is somewhat higher than that obtained on some other purer copper samples. Thermometer calibration curves so adjusted were taken for all the experiments with molybdenum and were then used to evaluate the data for the specific heat in both superconducting and normal states.

The Specimens

The different molybdenum samples and their composition are listed in Table I. Mo—1 was a single crystal, kindly loaned to us by Dr. D. Freeman of Linde Company, Tonawanda. It was etched at both ends so as to eliminate the strains resulting from the cutting of the sample.

Mo—2 was given to us by Dr. T. Geballe of Bell Telephone Laboratory and was made up of 3 crystals. The impurities of this sample were not given but the resistivity ratio showed that it was approximately as pure as Mo—1 or purer. The small size of both samples is the reason for the relatively large scatter in the experimental specific heat points.

Mo—3 was a single crystal; it was made the same

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[8] In another apparatus the magnetic susceptibility of chromium methylammonium had been measured directly against that of cerium magnesium nitrate between 0.08 and 1°K.

[9] H. R. O'Neal, Lawrence Radiation Laboratory, Report No. UCRL 10426 UC-4 Chemistry, University of California, 1963 (unpublished); G. Ahlers, J. Chem. Phys. **41**, 86 (1964); N. Phillips, Phys. Rev. **134**, A387 (1964).

TABLE I. Dimension, mass, resistivity ratio, and impurities for the four molybdenum samples.

	Mo−1	Mo−2	Mo−3	Mo−4
Mass (grams)	25.46	8.901	121.30	63.33
Number of moles	0.2681	0.09277	1.264	0.6599
Diameter (cm)	0.80	0.60	1.45	1.20
Length (cm)	5.16	3.32	7.25	5.75
Resistivity ratio	>1600	2700	313	1650

Impurities

Mo−1:[a]	ppm	Mo−4:[b]	ppm
C	4.7	C	5.0
O	2.8	O	1.0
W	0.1	Fe	5.0
Fe	0.01	N	0.5
Al	0.01	H	0.3
V	0.01		
Nb	0.01		
Si	0.001		

[a] Analysis by quantitative emission spectrography, carried out at the Linde Company.
[b] Typical chemical analysis of the triple-pass electron-beam zone-refined single-crystal rod, by Materials Research Corporation.

way as Mo−1 and also came from the Linde Company. Because of its large size it was less pure and showed a small resistivity ratio and a very broad superconducting transition.

Mo−4, also a single crystal, was purchased by Bell Telephone Laboratories from Materials Research Corporation and was kindly given to us through the efforts of Dr. N. R. Werthamer. The comparatively large mass of Mo−3 and Mo−4 should make these samples suitable for further specific heat measurements at temperatures below the liquid He^3 range.

The density at room temperatures was taken to be 10.20. This value was obtained from density measurements of Mo−1 made by Dr. D. C. Freeman and is consistent with the value of 10.23 measured on another sample by Clusius.[10] The density below 4°K was taken to be 0.3% higher, as calculated from published values of the coefficient of expansion.[11]

D. Experimental Procedure

Low-resolution specific heat measurements were made by supplying heat at a known rate to the sample for a measured interval of time, and determining the sample temperature before and after the heating interval. The temperature intervals were typically 10 mdeg at 0.4°K and 20 mdeg at 3°K. For the high-resolution measurements, heat was supplied to the sample at a constant rate and the temperature of the carbon resistance thermometers was continuously monitored by means of a chart recorder connected to the output of the phase-sensitive detector.[5] For a small enough ($\Delta R/R<0.01$) unbalance of the bridge, the detector system was linear to within 1%. The sensitivity of the bridge-detector system was automatically calibrated by observing the change of the chart recorder output every time the bridge was re-balanced by changing a decade resistor by, say, 100 Ω. Resistance points read from the chart record as a function of time were fed into the computer; and by using the calibration curve of the resistance thermometer, a series of temperature points-versus-time was obtained. An approximation to the temperature-versus-time curve was made by least-squares fitting a straight line to each group of, say, 10 points. The slope of each successive line was combined with the measured heating-rate data to yield the specific heat of the sample as a function of temperature. Appropriate corrections were made for the drift rate of the sample with no power applied to the heater. This drift rate was observed before and after every heating period for both high- and low-resolution measurements.

Separate runs were made to determine the heat capacity of the sample support, including the thermometers and the small amount of grease used for obtaining thermal contact. These addenda data were fitted to an equation of the form

$$C_{\text{addenda}}=a_0+a_1T+a_2T^2+\cdots a_5T^5. \qquad (3)$$

This expression was judged to fit the data with an uncertainty of about 5%. At 0.4°K the relative contribution of the addenda to the total heat capacity amounted to 34% for the smallest sample, Mo−2. At 3°K the relative contribution of the addenda amounted to 60% for Mo−2. Our final estimation of the errors is given in Table II.[12,13] The latent heat of the transition from the superconducting to the normal state was measured by increasing the field isothermally from a value well below H_c to a value just beyond H_c. It was also measured by supplying heat at a constant field and evaluating by successive approximations the area under the specific heat maximum. Both methods were described pre-

TABLE II. Results of measurements on normal molybdenum.

Source		Purity	$\gamma\left(\frac{\text{mJ}}{\text{mole-deg}^2}\right)$	Θ_D(°K)
Bryant and Keesom (1961)[a]		99.8%	1.93±0.03	427±26
		99.99%	1.91±0.02	458±15
Clusius and Franzosini (1959)[b]		99.99%	2.1 ±0.2	454
Rayne (1954)[c]		99.9%	2.20±0.10	...
Horowitz and Daunt (1953)[d]		99.9%	2.14±0.20	445
This work:				
Sample	Mo−1		1.81±0.04	382±10
	Mo−2		1.83±0.05	423±15
	Mo−3		1.89±0.02	461±10
	Mo−4		1.87±0.02	456±10

[a] Reference 12.
[b] Reference 10.
[c] Reference 13.
[d] Reference 15.

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[10] K. Clusius and P. Franzosini, Z. Naturforsch. **14a**, 99 (1959).
[11] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963), pp. 4–66, 2nd ed.
[12] C. A. Bryant and P. H. Keesom, J. Chem. Phys. **35**, 1149 (1961).
[13] J. Rayne, Phys. Rev. **95**, 1428 (1954).

viously.[5] The critical field curve was also obtained as before.[5]

RESULTS

A. Low-Resolution Measurements

The experimental data[14] for temperatures below 1.0°K are presented in Figs. 1(a) and (b) as a plot of C_n/T versus T^2. The data for the normal state specific heat between 4 and 0.4°K could be fitted to an equation of the form

$$C/T=\gamma+\alpha T^2, \qquad (4)$$

where C_n and T are the experimental values of specific heat and the corresponding temperature, and the coefficients γ and α are determined by a least-squares fit to the data. Values of γ, the electronic specific heat coefficient, and of the Debye temperature, $\Theta_D=(12\pi^4R/\alpha)^{1/3}$, where R is the gas constant, are listed in Table II, together with the values found by other investigators, for purposes of comparison. The present values of these coefficients are from 5 to 20% smaller than those previously reported, and may possibly be due to the higher purity of our samples. This hypothesis is further supported by the fact the least pure sample Mo—3 exhibited a γ and Θ_D which agreed more closely with the results of other investigators.[15] In niobium, another transition element, the presence of interstitial oxygen or nitrogen is known[16] to raise the value of γ and Θ_D.

Experimental values of the quantity $(C_s-C_n)/T$ for each sample were fitted to a power series expansion[17] in the temperature T. This expression was then integrated, using the usual thermodynamic relations to find the latent heat and critical field curve:

$$L(T)=T\int_T^{T_c}\frac{C_s+C_n}{T'}dT^1, \qquad (5)$$

$$H_c^2(T)=\frac{8\pi}{V}\int_T^{T_c}\frac{L(T')}{T^1}dT^1. \qquad (6)$$

Here T_c is the transition temperature in zero field and V is the molar volume. The resulting critical field curves are shown in Fig. 2, together with the ultrasonic absorption data of Horwitz and Bohm.[18] Deviations of our critical field curves from a parabolic law are similar to those predicted by BCS theory in the limit of weak coupling.[6] Our experimental results have too large an uncertainty, however, for any close agreement with the BCS theory to be much more than merely fortuitous. The experimental deviation from the parabolic law is shown in Fig. 3.

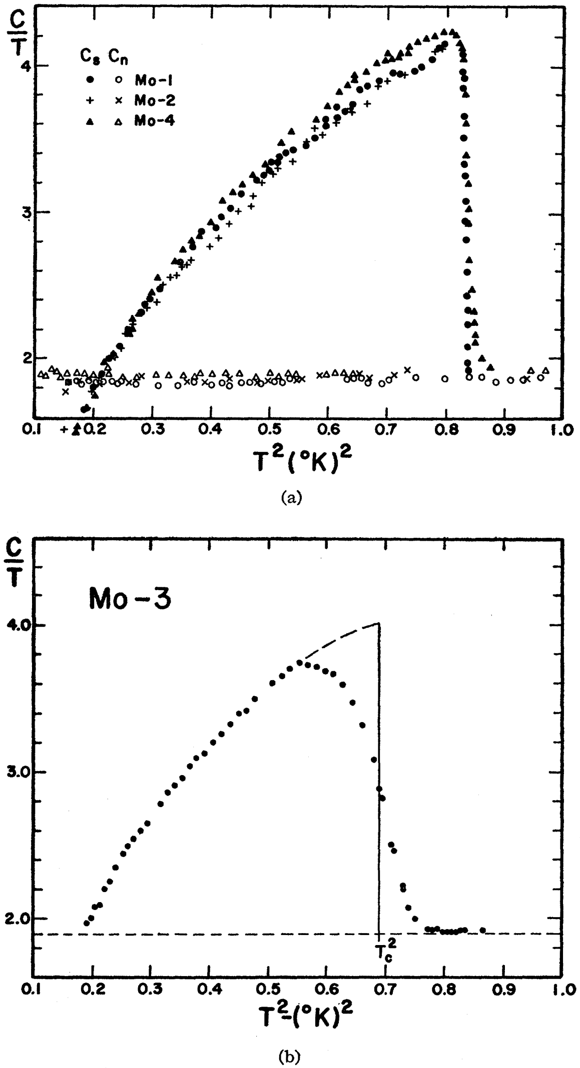

FIG. 1. The specific heat in the normal and superconducting state plotted as C/T versus T^2 for the four samples of molybdenum. Experimental points for the normal state in Mo—3 below $T_c^2=0.8(°K)^2$ are not shown in this graph, but they lie exactly on the dashed line.

In order to compare our experimental results for molybdenum with other predictions of the BCS theory, the specific heat of the electrons alone in the superconducting state must be obtained. This was accomplished by subtracting from the total measured heat capacity the amount which was judged to be the lattice contribution. The usual assumption was made that the specific heat of the lattice is the same for both normal and superconducting phases at any given temperature, so that the lattice contribution was given by the T^3 term in the measured normal-state specific heat.

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[14] Because of the very large number of experimental points for the four samples between 0.4 and 4.2°K, no tables of the specific heat, latent heat, and critical-field curve will be presented in this paper. A tabulation of these quantities is available upon request.

[15] M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953).

[16] A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. **127**, 1501 (1962).

[17] See, for instance, E. A. Lynton, *Superconductivity*, Methuen's Monographs on Physical Subjects (Methuen and Company Ltd., London, 1962), p. 19.

[18] N. H. Horowitz and H. V. Bohm, Phys. Rev. Letters **9**, 313 (1962).

Eliashberg[19] has suggested that an electron-phonon interaction in the normal state configuration of a metal will give rise to a term of the form $T^3 \ln T$ in the specific heat at low temperatures in addition to the familiar terms in T and T^3. The entropy associated with this interaction is given by

$$S = 3\lambda(s/v)\ln(\Theta_D/T)S_p,$$

where s is the velocity of sound, v the electron velocity at the Fermi surface, S_p the entropy of the lattice phonons, and $\lambda \approx 1$ is the electron-phonon coupling constant. Calculations show that this interaction is too small to be of consequence at the temperatures used in this experiment, and thus was disregarded. The results of C_{es} are plotted on a logarithmic scale as a function of T_c/T in Fig. 4(a) and 4(b), together with the expected BCS curve.[20] For temperatures near T_c, agreement is good, although the experimental $C_{es}/\gamma T_c$ for all the samples is systematically lower than the theoretical value, which tends to 2.43 at T_c. At the lowest temperatures, the upward deviation of the experimental data from the BCS curve is again larger than the probable error in the experimental determination and suggests the possibility of an anisotropy in the energy gap. Usually such deviations for superconductors with weak coupling appears for T_c/T larger than about 2–3.[21,6] This deviation is most pronounced for Mo—1 and Mo—2, the two purest samples. However Mo—3, the least pure sample has the same behavior as Mo—4, which is appreciably purer. It is possible that in molybdenum, as in aluminum, the purest sample shows the largest anisotropy of the energy gap.[21] For Mo—3 and Mo—4 this anisotropy, if any, is probably already smeared out. The observed behavior of the specific heat does not exclude the possibility that pure molybdenum has two distinct energy gaps, as suggested by Garland[22] for a "clean" transition element superconductor. However, on the basis of the present data, it does not seem possible to distinguish between the existence of two energy gaps, or one anisotropic gap. Experiments at still lower temperatures might be able to clarify this situation and are planned in this laboratory.

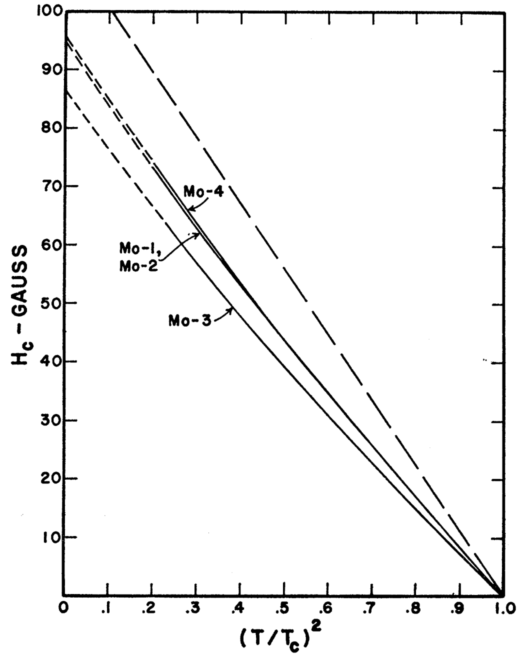

FIG. 2. The critical field of molybdenum as derived from specific-heat data via Eqs. (5) and (6). The dashed curve is that deduced by Horwitz and Bohm from acoustical measurements.

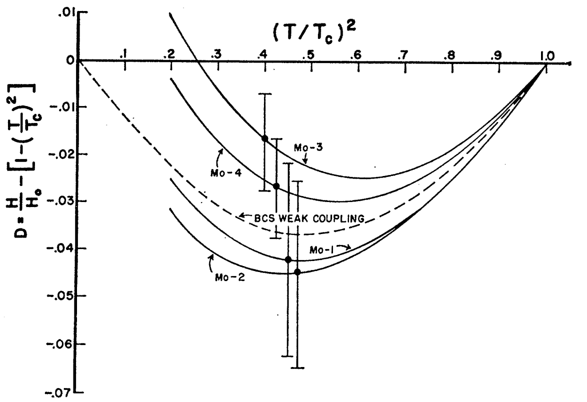

FIG. 3. The deviation of the critical field of molybdenum from that of a simple parabolic law. Dashed line: theoretical curve according to the BCS theory for superconductivity with weak coupling.

The value of the energy-gap parameter at $T = 0°\text{K}$, $2\epsilon_0/kT_c = (4\pi/\sqrt{3})[VH_c^2(0)/8\pi\gamma T_c^2]^{1/2}$, an expression derived by Goodman,[23] was estimated using the experimental values of T_c and γ, and the value of $H_0(0)$ deduced from the extrapolation of the critical field curve calculated from data on $C_s - C_n$. It is presented in Table III. The results give an average gap parameter

TABLE III. Results of measurements on superconducting molybdenum.

	Mo —1	Mo —2	Mo —3	Mo —4
T_c(°K)	0.915	0.918	0.83	0.917
Zero-field-transition width (mdeg)	3.8	<4	70	10
$(C_s - C_n)_{T=T_c}$ (mJ/mole-deg)	2.16 ± 0.07	2.16 ± 0.10	1.77 ± 0.04	2.18 ± 0.04
$-(dH_c/dT)_{T_c}$	178 ± 4	178 ± 5	169 ± 2	178 ± 2
H_0(G)	95 ± 5	95 ± 5	87 ± 3	96 ± 3
$\left(\frac{C_{es}}{\gamma T_c}\right)_{T_c}$	2.30 ± 0.10	2.29 ± 0.15	2.13 ± 0.10	2.26 ± 0.05
$\frac{2\epsilon_0}{kT_c}$	3.42 ± 0.15	3.40 ± 0.15	3.38 ± 0.10	3.40 ± 0.10

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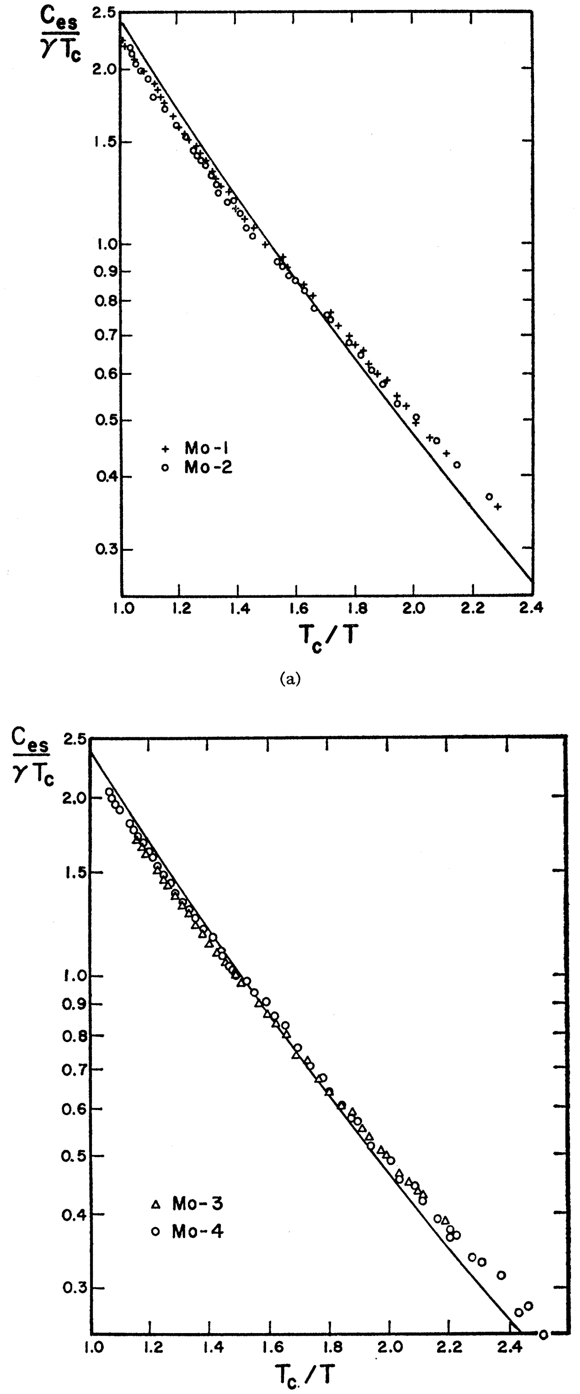
[19] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960) [English transl.: Soviet Phys.—JETP **11**, 696 (1960)].

[20] B. Mühlschlegel, Z. Physik **155**, 313 (1959).

[21] R. Geiser and B. B. Goodman, Phys. Letters **5**, 30 (1963).

[22] J. W. Garland, Jr., Phys. Rev. Letters **11**, 111, 114 (1963).

[23] B. B. Goodman, Compt. Rend. **246**, 3031 (1958).



(a)

(b)

FIG. 4. Electronic specific heat of molybdenum in the superconducting state, expressed as $(C_{es}/\gamma T_c)$ on a logarithmic scale versus T_c/T. The solid line is that calculated from the BCS theory.

which is consistent with the predicted value for a superconductor in the weak-coupling limit: $(2\epsilon_0/kT_c)=3.52$. Ultrasonic absorption measurements by Horwitz and Bohm[18] gave this parameter as 3.5±0.2.

B. High-Resolution Measurements

Results of the high-resolution measurements of the specific heat of sample Mo—1 in zero field are shown in Fig. 5. Two runs made by warming the sample through the transition showed very good agreement with two runs made by cooling the sample through the transition. In particular, there appeared to be no hysteresis and the transition in zero field was reversible. Total width of the transition was about 3.8 mdeg and the transition was centered about 0.915°K. There was no indication of an infinite discontinuity in the specific heat as the sample passed through the transition in zero field. This is an agreement with measurements on other superconductors.[5,24,25]

Although high-resolution measurements were not made on the other samples, enough data were taken to determine that the zero-field transition in Mo—2 ocurred at a temperature $T_c=0.918$°K and was less than four mdeg wide; for Mo—3 the transition was centered at $T_c=0.830$°K and was approximately 70 mdeg wide; and for Mo—4, $T_c=0.917$°K, and the transition width was 10 mdeg.

The transition temperature for samples 1, 2, and 4 is in good agreement with the values 0.918°K and 0.917°K reported by Matthias and co-workers[26] for two small samples of very pure molybdenum of natural isotopic composition. These authors also found the limiting transition width to be approximately 1.2 mdeg. As our samples are larger than those of Matthias, and consequently less perfect, the transition widths for Mo—1 and Mo—2 are larger.

The critical field curve was determined near $H_c=0$ by direct measurement of a transition temperature corresponding to each different value of an applied field. Since the transition does not cause an abrupt

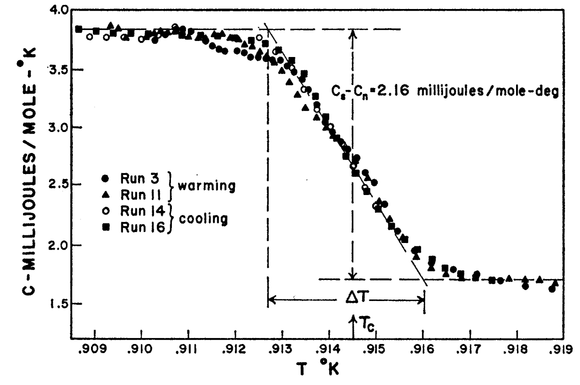


FIG. 5. High-resolution specific heat of Mo—1 in "zero" field showing the results of warming and cooling through the transition.

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[24] M. J. Buckingham and W. M. Fairbank, *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1961), Vol. III.

[25] J. F. Cochran, Ann. Phys. **19**, 186 (1962).

[26] B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. **129**, 1025 (1963).

change in the observed specific heat, but rather affects the specific heat over a finite temperature interval, the chief difficulty was to determine a unique temperature to be associated with a particular value of the magnetic field. Thus, starting at T_1, the low-temperature end of the transition, the specific heat was observed to rise from the superconducting-state value C_s, go through a large peak (corresponding to the absorption of latent heat), and then abruptly decrease to the normal-state value C_n at the temperature T_2. The specific heat curves for several different values of the applied magnetic field are shown in Fig. 6. The peak is not as smooth as for aluminum.[5] During the transition, sudden jumps in the temperature were observed, which may indicate transition of individual domains in the sample. For any temperature T within the transition, a fraction $x(T)$ of the sample will have switched from the superconducting to the normal state. The fraction $x(T)$ is proportional to the latent heat absorbed from T_1 to T, and is the area of the "bump" in the specific heat curve from T_1 to T. This fraction is given by

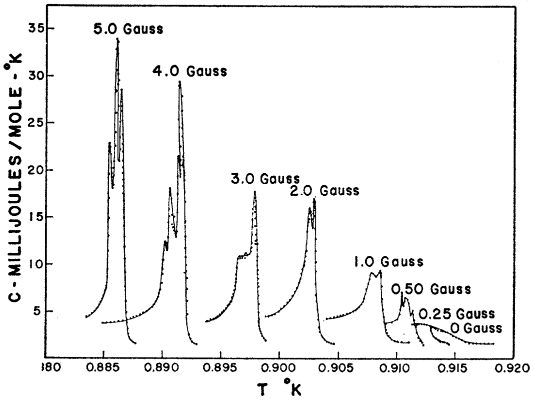

FIG. 6. Specific heat in small magnetic fields near the transition T_c.

$$x(T)=\int_{T_1}^{T} ydT' \Big/ \int_{T_1}^{T_2} ydT',$$

where $y=[C(T')-x(T')C_n-\{1-x(T')\}C_s]$,

where $C(T)$ is the experimentally measured value of the specific heat within the transition at temperature T. This equation was solved by successive approximations, using the digital computer, and the resulting values of $x(T)$ were plotted as a function of temperature, as was done in Figs. 4 and 5 of Ref. 5. The transition temperature was then determined from these curves as before. The critical field curve, obtained in this way (Fig. 8), falls in the center of the experimentally observed zero-field transition upon extrapolation, as one would expect.

Directly measured values of the latent heat, obtained isothermally and at constant magnetic field, and the critical field curve were compared with values obtained from Eqs. (5) and (6) using the high-resolution specific-heat data. These latent heat data could be used in Eq. (6) to obtain still another set of values for the critical field curve. Thus we have three latent heat curves and three critical field curves to be compared for magnetic fields near $H=0$. These curves are shown in Figs. (7) and (8). The critical field curves are all in good agreement. The latent heat obtained isothermally was systematically smaller by a few percent than that obtained at constant field and that calculated from Eq. (5). All of these measured quantities are, however, thermodynamically consistent to within the experimental error.

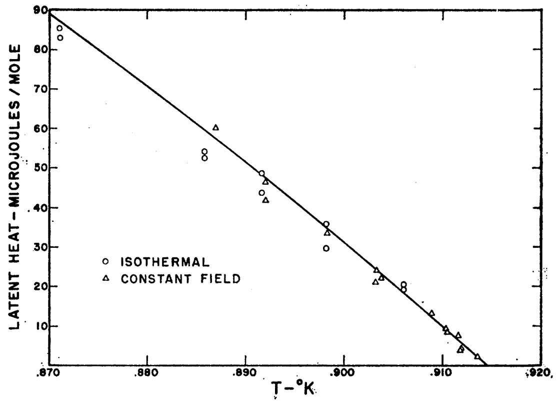

FIG. 7. Latent heat near T_c.

A concise way of comparing the experimental values of specific heat, latent heat, and critical field is through the parameter $(dH_c/dT)_{H=0}$ as was done previously.[5] The results of these three determinations for sample Mo−1 are:

From the specific heat: $(dH_c/dT)_{T_c}=-178\pm4$ G/deg;

From the latent heat: $=-176\pm3$ G/deg;

From the critical field: $=-180\pm3$ G/deg.

Agreement is seen to be reasonable within experimental

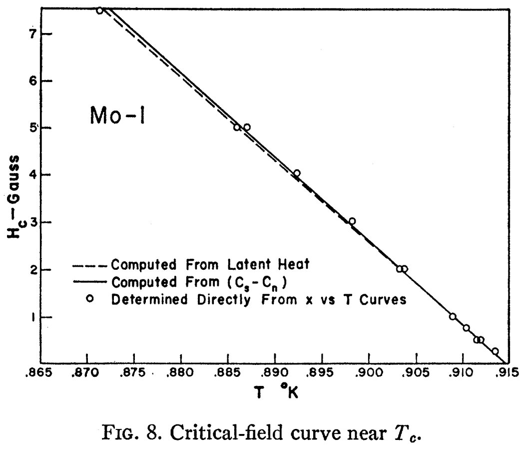

FIG. 8. Critical-field curve near T_c.

error. This thermodynamic consistency provides increased confidence in the reliability of the measurements.

IV. CONCLUSIONS

The thermodynamic properties of the three purest samples of molybdenum are very consistent in both the normal and the superconducting state. Pure molybdenum appears to have the reversible transition of a type I superconductor. The transition width is apparently quite sensitive to very small traces of impurities, which also seem to affect the specific heat in both normal and superconducting states as well. We have deduced several thermodynamic properties from specific heat measurements in the neighborhood of and well below the critical temperature and compared them with the theoretical predictions. The average width of the energy gap at 0°K as deduced from our specific heat measurements is consistent with the BCS value. Anisotropy of the energy gap or possible existence of two gaps may be indicated by the experimental data for C_{es} at the lowest temperatures, which are larger than the values from the BCS theory. A λ-type anomaly in the transition in zero field could not be detected, in agreement with the measurements on other superconductors.

ACKNOWLEDGMENTS

We acknowledge part-time financial support of one of us (D.G.O.) by the Duke University Council. We are very grateful to Dr. D. Freeman at the Linde Company, Tonawanda Laboratory, Dr. Ted Geballe and Dr. N. R. Werthamer at Bell Telephone Laboratories, for their efforts to make the molybdenum samples available to us. We are indebted to Dr. C. Grimes and Dr. W. A. Reed at Bell Telephone Laboratories for measuring the resistivity ratios of these samples. We are indebted to R. Gonano for his help during some of the experiments. The theoretical advice of Dr. N. R. Werthamer has been very much appreciated.

PHYSICAL REVIEW VOLUME 138, NUMBER 6A 14 JUNE 1965

Thermal Mixing between Spin Systems in Solids

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(Received 25 January 1965)

The present work is a study of thermal mixing in zero field between protons and bromine nuclei in paradibromobenzene, induced by rf irradiation at a frequency close to the bromine quadrupole resonance frequency. Experiments have been conducted at 77 and 4.2°K. This mixing leads to the cooling of the dipole-dipole interactions to a temperature which depends on the relative couplings to the lattice of the different interactions—dipolar and quadrupolar—experienced by the spin system. The ordering of the dipolar interactions is transferred to Zeeman interactions by adiabatic magnetization, which results in an enhanced proton polarization with respect to its thermal-equilibrium value. A detailed theory of the thermal mixing, together with experimental results obtained with paradichlorobenzene, has been published in a preceding article. The present work pays special attention to the dynamics of the evolution of the spin system during the thermal contact. This evolution proceeds from two distinct phenomena: The first is the establishment of a spin temperature in the rotating frame by rf-induced thermal mixing between dipole-dipole and quadrupole interactions. The second is a variation of this temperature at a rate and toward a steady-state limit determined by the respective spin-lattice relaxation times of the dipole-dipole and quadrupole interactions. The experiments performed at 4.2°K with paradibromobenzene verify this two-step evolution. They also demonstrate that even very low concentrations of paramagnetic impurities provide the dominant relaxation mechanism for the dipole-dipole interactions, resulting in a drastic decrease of the dynamic polarizations obtainable by this method.

I. INTRODUCTION

In a preceding article[1] with A. Landesman, referred to hereafter as I, we have presented a method of dynamic polarization of a nuclear spin species I, in solids, through its thermal mixing in zero field with a second spin species S which is subjected to quadrupole interactions. One of the features of this method, on which emphasis was given throughout the analysis made in (I), is that under suitable conditions—gyromagnetic ratio γ_S of the spins S smaller than the gyromagnetic ratio γ_I of the spins I, and spin-lattice relaxation entirely originating from the coupling of the lattice with the spins S only—the resulting polarizations are larger than the maximum polarization which can be expected from a "solid effect," i.e., the final ratio of populations between the levels of the spins I is larger than the Boltzmann ratio $\hbar\omega_Q/kT$ corresponding to the quadrupole splitting of the spins S. Experiments performed on paradichlorobenzene at liquid-nitrogen temperature qualitatively verified the correctness of the theory and

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[1] M. Goldman and A. Landesman, Phys. Rev. **132**, 610 (1963).