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Heat Capacity in the Normal and Superconducting States and Critical Field of Niobium*†

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The heat capacity of a vacuum-annealed sample of niobium has been determined in the temperature range 1.5 to 30°K. The heat capacity measurements in the normal state below the transition temperature were carried out in magnetic fields up to 4130 gauss. The effect of vacuum annealing on the heat capacity, transition temperature, and critical field was determined in an effort to obtain a so-called ideal superconductor. After the initial annealing, within experimental error, the heat capacity in the superconducting state was found to be independent of further treatment. In the normal state the heat capacity (C_n) can be represented by the relation

$$C_n=0.0018T+464.4(T/\theta)^3,$$

where θ varies from 256 to 320 degrees depending on the temperature for the best annealed sample. No simple relationship holds for the heat capacity in the superconducting state. The heat capacity data could not be fitted to any existing corresponding state theory for superconductors.

The zero-field transition temperature (T_c) and the critical field (H_c) were found to depend on the extent of annealing. For $T_c=9.07$°K, $(dH_c/dT)_{T=T_c}=1148$ gauss deg^{-1} whereas for $T_c=9.17$°K, the highest transition temperature measured, $(dH_c/dT)_{T=T_c}=734$ gauss deg^{-1}. From the heat capacity data $(dH_c/dT)_{T=T_c}=415$ gauss deg^{-1} and H_0, the critical field at absolute zero$=1944$ gauss. It was not possible by vacuum annealing even at 2100°C to obtain an "ideal" superconductor.

INTRODUCTION

THE thermodynamic treatment of the superconducting phase transition in metals, in the presence of a magnetic field, requires that the difference in the free energies of the normal and superconducting phases be proportional to the square of the critical magnetic field. Thus the differences in the entropy between the two phases as well as the heat capacities can be deduced from the critical field curve. Comparison of critical-field data with calorimetric data has shown that the agreement is generally good in the case of the so-called "soft superconductors." Considerable discrepancies however have been found for "hard superconductors" whose magnetic properties depend strongly on the physical and chemical condition of the specimen. This was shown by Webber[1] and by Wexler and Corak,[2] who found that the hardness of these metals arise from inhomogeneous strains set up in the lattice either by mechanical work or by impurities, particularly carbon, oxygen, and nitrogen, which at low concentrations are present in the lattice interstitially. Annealing at elevated temperatures and high vacuum can remove mechanical strains or gaseous contaminants but not, in general, the strains due to interstitially located foreign atoms.

An attempt has been made in this laboratory to investigate both the calorimetric and magnetic behavior of the hard superconductors niobium and tantalum after careful annealing and degassing in high vacuum at elevated temperatures. The results on niobium are reported in this paper. During the course of this investigation the heat capacity of niobium in the normal and superconducting state was reported by Brown, Zemansky, and Boorse.[3] No attempt, however, was made in their research to determine the effect of repeated annealing and purification of the sample on the thermodynamic properties.

APPARATUS

1. Calorimeter

A Nernst-type vacuum calorimeter shown in Fig. 1 was used in this research. The calorimeter proper A was made of O.F.H.C. copper in the shape of a cylindrical round cap with an o.d. of 1 in. and i.d. of approximately 0.70 in. The inside of this cap was threaded so that a metal sample could easily be attached. Apiezon N stopcock grease was used in the threads for thermal contact. A bare carbon resistor, used as a resistance thermometer, was coated with a thin film of Bakelite and inserted in the upper part of the calorimeter B. G.E. 7031 adhesive was used for thermal contact. On the outside of the copper calorimeter a constantan heater C was wound bifiliarly (No. 36 B & S Driver Harris "Advance" double nylon insulated). The room temperature resistance of this heater was approximately 85 ohms. A thin layer of highly polished copper foil 0.001 in. thick was wrapped around the heater. This was to serve as a radiation shield.

All the leads from the calorimeter (No. 34 B & S Driver Harris double nylon insulated manganin wire)

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[1] R. T. Webber, Phys. Rev. 72, 1241 (1947).

[2] A. Wexler and W. S. Corak, Phys. Rev. 85, 85 (1952).

[3] Brown, Zemansky, and Boorse, Phys. Rev. 92, 52 (1953).

passed through the cylindrical lead block *D* and a copper block *F*. The latter was soldered to the vacuum jacket *G* so that it made good thermal contact with the bath. The copper block *F* served to remove the heat transmitted through the leads from the top of the calorimeter as well as a radiation shield. Since the bath temperature during a run was always somewhat lower than the calorimeter temperature the lead block *D* served to reduce the heat leak through the manganin leads. This block was approximately 1 in. in diameter and $\frac{1}{4}$ in. long and was wound bifiliarly with a constantan heater so that its temperature could be controlled.

The calorimeter was surrounded by a cylindrical brass vacuum jacket *G* approximately $1\frac{1}{2}$ in. diameter and $5\frac{1}{2}$ in. long. A monel pumping tube approximately $\frac{3}{8}$ in. in diameter was soldered to the vacuum jacket. The whole calorimetric assembly was placed in a Pyrex Dewar vessel 40 in. long and $2\frac{3}{4}$ in. o.d. into which liquid helium or hydrogen could be transferred. This was surrounded in turn by a somewhat large liquid nitrogen Dewar into which an air core electromagnet could be positioned for both the calorimetric and magnetic investigations. The magnetic field was parallel to the sample cylinder axis. This liquid-nitrogen-cooled magnet was a modified version of the magnet described by Fritz and Johnston,[4] Formex-coated copper wire (B & S No. 21) having been used in the construction rather than cotton-insulated wire. The magnet gave a field of 200±2 gauss per ampere at its center. The current source for the magnet consisted of twenty-four 8-volt submarine batteries of 500 ampere hours capacity. The maximum field strength obtainable without serious overheating of the magnet was approximately 5600 gauss.

For the calorimetric measurements above 9°K (liquid hydrogen in the small Pyrex Dewar) the calorimeter was cooled by means of a small amount of helium exchange gas (10^{-2}–10^{-3} mm Hg) inside the vacuum jacket. After the calorimeter had equilibrated with the bath, good thermal isolation of the calorimeter was achieved by pumping in the vacuum jacket for approximately two hours. For the measurements below 9°K (liquid helium in the small Pyrex Dewar) sufficient thermal isolation could never be achieved by the above procedure to enable any reasonable measurements particularly in the range 1.5 to 3°K. (The heat capacity of the niobium sample at 1.5° is approximately 0.6×10^{-4} cal deg^{-1}.) To avoid this difficulty a stainless steel capillary *E*, 0.020 in. i.d. and 0.036 in. o.d., was soldered to the top of the calorimeter. It passes through the lead, vacuum jacket (making good thermal contact with both), and liquid helium refrigerant to a helium gas supply. From earlier experiments[5] it was found that such a capillary containing gaseous helium considerably below its saturation pressure and in contact with liquid helium below the λ point, conducts heat very rapidly (transport by superfluid adsorbed film). Furthermore, if the gas pressure in the capillary is reduced sharply by pumping for only a few minutes, thermal contact between the liquid helium in the bath and the capillary becomes negligible. In the case of the calorimeter it was found that when the liquid helium temperature was reduced to 1.5°K, helium at approximately 10^{-2}-in. pressure in the capillary reduced the temperature of the calorimeter from 9°K to 1.5°K in a period of $\frac{1}{2}$ hour. Excellent thermal isolation of the calorimeter was achieved by pumping the capillary for approximately 10 minutes. This was indicated by the linear change in temperature of the calorimeter in the fore and after periods of a run due to the energy input of the resistance thermometer and a small amount of heat leak through the leads.

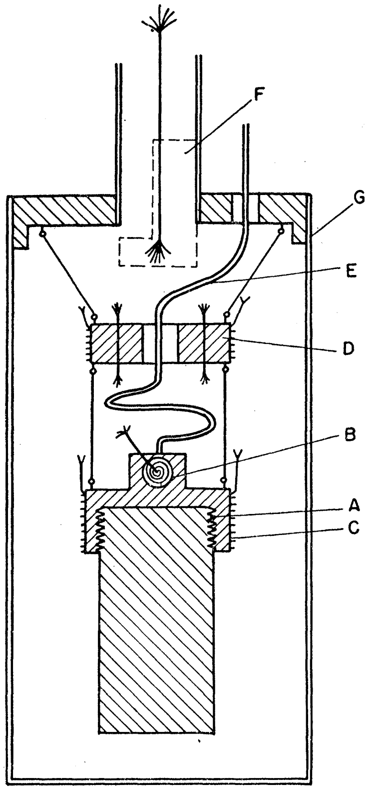

FIG. 1. Calorimeter.

2. Electrical Circuits and Timing

The circuits used in this research were similar to those used by Gibson and Giauque[6] except that the heater current and voltage were measured directly by a type B Rubicon potentiometer with a maximum range of 1.6 volts. During the first part of the investigation a

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[4] J. J. Fritz and H. L. Johnston, Rev. Sci. Instr. **21**, 416 (1950).

[5] White, Chou, and Johnston, J. Chem. Phys. **20**, 198 (1952).

[6] G. E. Gibson and W. F. Giauque, J. Am. Chem. Soc. **45**, 93 (1923).

modified version of the timer designed by Johnston[7] was used. In the later runs a stopwatch checked against a jeweler's electric timer was used.

PROCEDURE

The experimental methods used in the measurements of the heat capacity followed those commonly used and described extensively in the literature. Only those features specific or unique to the investigation will be given. A new method has been used to determine the threshold field at various temperatures. This is discussed in detail below.

1. Thermometry

For the measurement of temperature, a 1-watt 40-ohm carbon resistor was used as a thermometer. It was produced by the Speer Resistor Company and differed from the Allen and Bradley in the dR/dT characteristics. Some values are tabulated below:

T°K	R (ohm)	dR/dT (ohm deg^{-1})
20	75	1
15	80	1.3
10	87	2.0
4.2	116	10
1.3	170	40

In the range 10 to 20°K the carbon thermometer was calibrated by direct comparison with the vapor pressure of solid and liquid hydrogen read on a mercury and dioctyl phthalate manometers with a Gaertner cathetometer. The vapor pressure of solid and liquid hydrogen were converted to temperatures using the vapor pressure equations of Scott and Brickwedde.[8] A calibration was usually made after each series of heat capacity determinations in the temperature range. In the range 1.5 to 4°K the carbon thermometer was calibrated against the vapor pressure of helium, and converted to temperatures by using a table compiled by the Royal Society Mond Laboratory[9] known as the 1948 temperature scale (T_{48}). Since the completion of this research a new temperature scale (T_{55E}) has been published by Clement, Logan, and Gaffney.[10] The data have been corrected on the basis of this new scale.

The resistance-temperature relation for the carbon resistor in both the liquid helium and solid and liquid hydrogen ranges was quite simple. A large scale plot of $\log_{10}R$ *vs* $\log_{10}T$ gave approximately two straight lines which were joined graphically. The deviations from a straight line were then tabulated at intervals of 0.05 in $\log_{10}R$ and the second difference numerically smoothed. Temperatures calculated from this table reproduced the original data to within ±0.001 degree. The calibration of the resistance thermometer was found to be independent of an external magnetic field.

2. Heat Capacity Measurements in a Magnetic Field

The magnetic field was always applied after the sample had cooled down to the lowest temperature which was approximately 1.3°K. The procedure employed in the heat capacity measurements was identical to that in zero field. The magnetic field was held constant throughout the run to within ±0.03% by manual control of the current in the solenoid.

3. Determination of the Critical Fields as a Function of Temperature

For a direct comparison of the magnetic properties of the sample with those computed from the calorimetric data it was felt necessary to perform the critical field determination on the same sample as in the calorimetric experiments and without further handling of the sample. As a result of this the critical field as well as the transition temperature in zero field were determined in the calorimeter from heating curves. A break occurs, in the former case, due to the latent heat which is supplied during the transition interval in a magnetic field (the interval being quite large due to the shape of the sample) and in the latter due to the difference in heat capacity between the normal and superconducting states.

The experimental procedure was as follows: the sample was cooled down to a few tenths of a degree below the transition temperature and a constant magnet field applied. It was then slowly heated at constant energy input. The temperature of the sample was noted every 15 seconds until the slope of the temperature-time curve corresponded to that of the sample in the normal state. In Fig. 2 a heating curve for the zero field is shown. The temperature of the sample, expressed in microvolts, is plotted as a function of time which is directly proportional to the energy input. An abrupt change in slope occurs at 9.17°K, the zero-field transition temperature. From the slope before and after the transition temperature, the difference in heat capacity between the sample in the normal and superconducting states can be calculated. This is found to be identical with that obtained from the heat capacity determinations.

In Fig. 3 the heating curve in a field of 198 gauss is given; a break occurs at 8.86°K. Since the slope of the curve above 8.86°K corresponds to that for the sample in the normal state, it follows that the above magnetic field is sufficient to destroy completely the superconductivity at that temperature.

PURITY AND TREATMENT OF SAMPLE

The niobium sample used in this research was a cylinder approximately $\frac{3}{4}$ in. in diameter and 1 in. long obtained in 1948 from Fansteel Metallurgical Corporation, the only commercial source of the high grade

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[7] H. L. Johnston, Rev. Sci. Instr. **17**, 381 (1928).

[8] Woolley, Scott, and Brickwedde, J. Research Natl. Bur. Standards **41**, 379 (1948).

[9] H. van Dijk and D. Shoenberg, Nature **164**, 141 (1949).

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

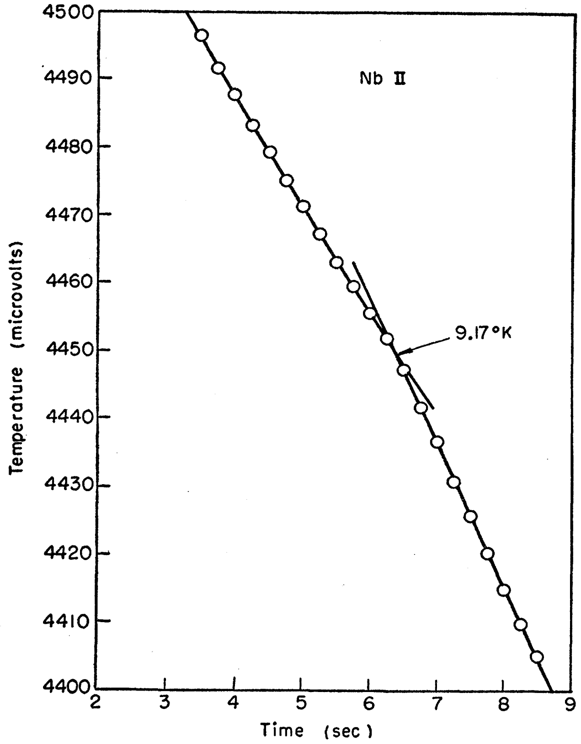

FIG. 2. Zero-field transition of Nb II.

metal. It was delivered as annealed, strain free, and of 99.8% purity, the major impurity being tantalum.[11] This sample was probably identical to the Fansteel sample employed by Boorse *et al.*[3,12] in their calorimetric and magnetic investigations. Their observed zero-field transition temperatures were 8.70 and 8.65°K, respectively.

It had been observed earlier in this laboratory that both tantalum or niobium obtained from the Fansteel Corporation, when heated above 1000°C, gave off considerable quantities of noncondensible gases (probably N_2 and O_2). An attempt was therefore made to improve the quality of the niobium sample by vacuum annealing, thus removing the gaseous contaminants as well as relieving any internal stresses. It was, however, found impossible by this procedure to reduce the niobium to a so-called "ideal" superconductor characteristic of the soft superconductors.

The niobium sample was annealed and degassed three times at successively higher temperatures in a water-cooled brass vacuum furnace described by Edwards, Johnston, and Blackburn.[13] The residual pressure in the furnace during the annealing was always less than 5×10^{-6} mm Hg.

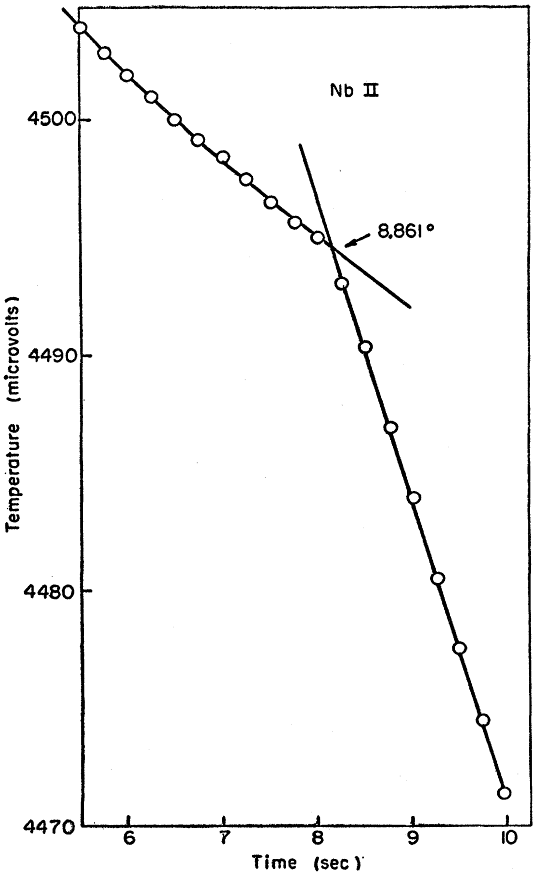

FIG. 3. Transition of Nb II in a field of 198 gauss.

Annealing	I:	1200–1600°C,	8 hours;
	II:	1450–2100°C,	20 hours;
	III:	2100°C,	8 hours.

The niobium sample after the first, second, and third annealing will be referred to subsequently in the text—as Nb I, Nb II, and Nb III, respectively.

EXPERIMENTAL RESULTS

1. Heat Capacity

The experimental results for samples Nb I and Nb II are given in Tables I and II. Only a few heat-capacity measurements were made using Nb III, since it was found that its zero-field transition temperature was identical to that of Nb II. These results, which covered only the temperature range 1.59 to 1.87°K, are given in Table III. Because of the controversy concerning the thermodynamic temperature scale in the liquid helium range, the heat capacity results in this temperature range is reported with both the 1948 $(T_{48})^9$ and 1955 $(T_{55E})^{10}$ temperature scales. The heat-capacity data are plotted in Figs. 4 and 5.

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[11] Fansteel Columbium-Fansteel Metallurgical Corporation, N. Chicago, Illinois (1946), 12 pp.

[12] Cook, Zemansky, and Boorse, Phys. Rev. **80**, 737 (1950).

[13] Edwards, Johnston, and Blackburn, J. Am. Chem. Soc. **74**, 1539 (1952).

TABLE I. Heat capacity of Nb I.

Run No. 1. Zero magnetic field

T_{55E} (°K)	$C_{55E}\times10^4$ (cal deg^{-1} mole^{-1})	T_{48} (°K)	$C_{48}\times10^4$ (cal deg^{-1} mole^{-1})
2.039	3.85	2.040	3.87
2.297	6.64	2.301	6.61
2.425	7.46	2.429	7.49
2.481	8.61	2.485	8.64
2.725	14.1	2.729	14.2
2.821	17.0	2.825	17.1
3.045	21.8	3.048	22.0
3.690	48.4	3.691	48.7
4.009	62.1	4.009	62.6
4.310	78.1	4.307	78.7
4.740	106.0	4.736	106.3
5.212	140.0	5.207	140.0
5.788	193.2	5.786	192.6
6.383	254.4	5.786	
7.012	335.6		
7.637	437.4	same as T_{55E}	
8.202	532.3		
10.081	508.2		
10.875	600.3		

Run No. 2. Zero magnetic field

T (°K)	$C_p\times10^4$ (cal deg^{-1} mole^{-1})
8.804	655.3
8.932	711.5
9.030	624.2
9.712	462.8
9.951	487.7
10.300	527.7
10.757	578.4
11.406	662.4
12.034	750.1
12.740	846.4
13.538	976.2
14.594	1158.1
15.648	1369.0
16.654	1564.8
17.680	1792.8
18.903	2138.8
20.138	2617.0
21.574	2995.2
22.979	3631.0
24.323	4233.3
25.859	5131.2
27.724	6175.0
29.450	7425.1

Run No. 3. Magnetic field 2640 gauss

T (°K)	$C_p\times10^4$ (cal deg^{-1} mole^{-1})
5.078	192.5
5.125	176.1
6.440	197.7
7.061	237.3
7.734	300.3
8.469	354.5
9.138	415.9
10.121	520.3
10.944	611.8

Run No. 4. Magnetic field 3000 gauss

T (°K)	$C_p\times10^4$ (cal deg^{-1} mole^{-1})
5.267	169.7
7.313	263.5
9.001	398.5
9.853	481.8
10.744	584.4

TABLE II. Heat capacity of Nb II.

T_{55E} (°K)	$C_{55E}\times10^4$ (cal deg^{-1} mole^{-1})	T_{48} (°K)	$C_{48}\times10^4$ (cal deg^{-1} mole^{-1})
Run No. 1. Zero magnetic field			
1.467	0.66	1.469	0.66
1.732	1.25	1.729	1.29
1.863	2.34	1.865	2.36
2.081	3.97	2.082	3.98
2.314	6.65	2.318	6.61
2.519	9.42	2.525	9.46
2.788	14.8	2.794	15.0
3.146	24.2	3.149	24.5
3.602	39.4	3.603	39.8
3.929	55.9	3.928	56.5
4.348	78.4	4.344	79.1
4.809	111.6	4.804	111.9
5.305	150.7	5.300	150.2
6.017	220.0	6.015	219.2
6.923	334.0	6.923	333.1
7.857	472.3		
8.468	581.1		
8.763	650.1		
9.927	486.5	same as T_{55E}	
10.015	493.5		
11.132	644.4		
Run No. 2. Magnetic field 4130 gauss			
1.353	27.0	1.353	27.1
1.466	25.1	1.467	24.9
1.620	32.0	1.623	31.6
1.770	33.6	1.774	33.6
1.961	38.4	1.967	37.9
2.217	44.2	2.229	42.8
2.402	48.9	2.418	47.8
2.596	50.7	2.613	50.9
2.940	59.5	2.954	61.0
3.250	65.3	3.258	66.6
3.579	76.4	3.583	77.0
3.929	86.0	3.933	85.9
4.436	99.5	4.439	99.8
4.877	120.9	4.819	121.7
5.392	139.3	5.392	139.5
6.059	176.0		
6.887	222.3	same as T_{55E}	
7.921	291.9		
9.110	390.6		

2. Critical Field

The zero-field transition temperatures and the critical-field data for Nb I, II, and III are given in Table IV. The upper limit of the width of the zero-field transition intervals, for all three samples, could be estimated from the heating curves. For Nb I it was found to be less than ±0.05 degree, whereas for Nb II and III it was less than ±0.03 degree.

TABLE III. Heat capacity of Nb III.

Zero magnetic field

T_{55E} (°K)	$C_{55E}\times10^4$ (cal deg^{-1} mole^{-1})	T_{48} (°K)	$C_{48}\times10^4$ (cal deg^{-1} mole^{-1})
1.585	1.20	1.587	1.21
1.699	1.45	1.703	1.46
1.789	1.76	1.793	1.78
1.863	2.28	1.868	2.30

3. Probable Errors

The heat capacity (in cal deg^{-1} mole^{-1}) is computed from the experimental data by using the expression

$$C_p=\frac{1}{n}\left(\frac{EIt}{J\Delta T}-C_{\mathrm{blk}}\right),$$

where E is the voltage across the heater, I the current in amperes through heater during energy input interval, t the heating time in seconds, ΔT the change in temperature due to heating, J the value of the absolute calorie defined as 4.1840 absolute joules, C_{blk} the heat capacity of the copper block supporting the niobium sample, heater, and resistant thermometer, and n the number of moles of niobium. The quantities E and I were measured with a precision of better than 0.1%. When the time t was measured by using a stopwatch, it was measured to within ±0.1 sec so that the maximum uncertainty for the shortest heating period 60 sec, is ±0.2%. C_{blk} was determined experimentally before the niobium sample was attached. In the temperature range 1.5 to 4.5°K. C_{blk} is given by the relation

$$C_{\mathrm{blk}}\times 10^4=0.791T+0.08781T^3.$$

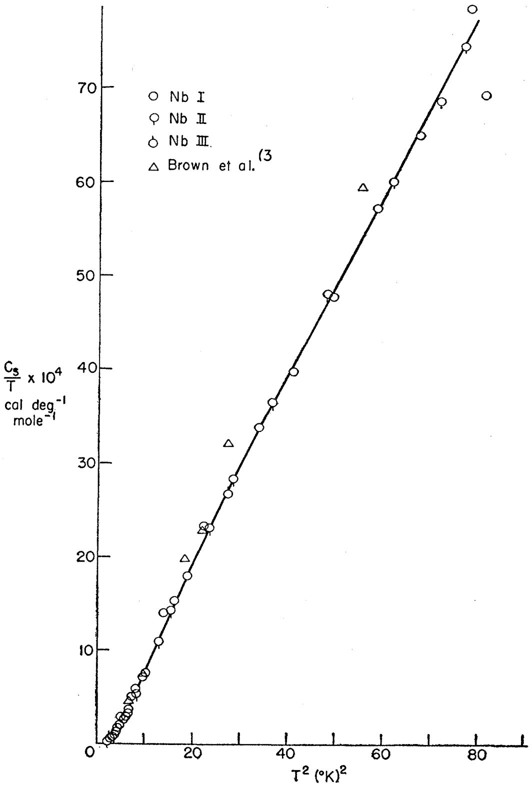

FIG. 4. Heat capacity of Nb in the superconducting state.

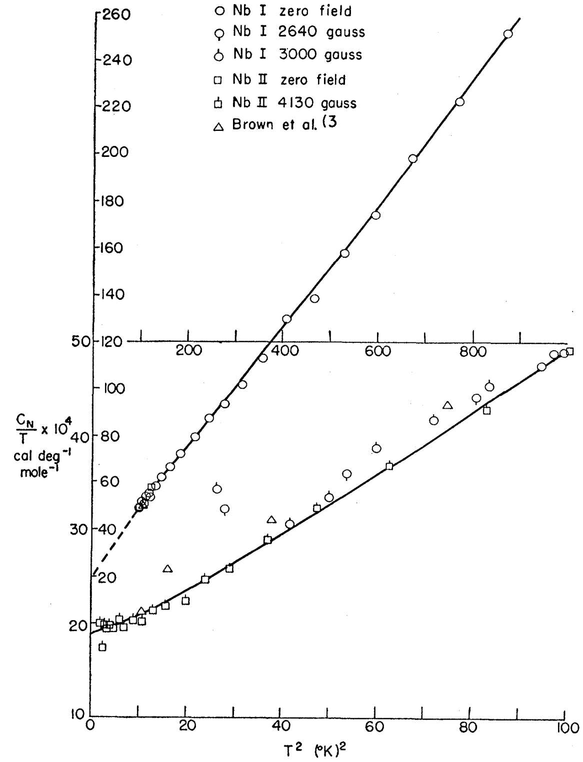

FIG. 5. Heat capacity of Nb in the normal state.

From 4.5 to 9°K,

$$C_{\mathrm{blk}}\times 10^4=1.038T+0.7557T^3.$$

Above 9°K, C_{blk} was tabulated at every degree and numerically interpolated. At 9.795°K, $C_{\mathrm{blk}}=0.008194$ cal deg^{-1}, at 24.851°K, $C_{\mathrm{blk}}=0.10433$ cal deg^{-1}. C_{blk} was approximately equivalent to the heat capacity of 0.46 mole of copper. Since the niobium sample used in the experiments was approximately 0.5 mole, the percentage of the total measured heat capacity due to

TABLE IV. Critical field as a function of temperature.

Temperature (°K)	Critical field (gauss)
Nb I	
9.07	0
5.9	2640
5.1	3000
Nb II	
9.17	0
9.04	98
8.86	198
8.68	297
8.45	509
7.96	798
7.18	1262
6.57	1624
5.62	2189
Nb III	
9.17	0
8.06	740

C_{blk} was approximately as follows:

At 1.5°K (superconducting state),	70%;
1.5°K (normal state),	10%;
4°K (superconducting state),	24%;
4°K (normal state),	18%;
10°K,	25%;
20°K,	30%.

The uncertainty of C_{blk} at 1.5°K, 4°K, 10°K, and 20°K is approximately 5%, 0.3%, 0.2%, and 0.2%, respectively. Thus the uncertainty in the heat capacity of niobium due to this effect is of the order of 3.5% at 1.5°K, in the superconducting state, but only 0.5% in the normal state. Above 2°K the uncertainty is less than 0.1%.

The temperature difference ΔT was obtained by graphical extrapolation of the temperature drifts before and after the heating interval. In almost all cases these were found to be linear with time, permitting an extrapolation precision of 0.1%.

If the errors discussed above were all cumulative and of the same sign, the expected precision at 1.5°K, where the shortest heating interval is used, would be ±5.4% in the superconducting state and ±1.0% in the normal state. At 2°K, however, it would only be ±0.5%, and would reach a minimum of approximately ±0.3% at higher temperatures. The average deviation of the experimental data from a smooth curve is consistant with precision measure discussed above.

The uncertainty in the zero-field transition temperatures from the heating curves is estimated to be ±0.01 degree. The uncertainty of the applied magnetic field is ±1%.

DISCUSSION OF RESULTS

1. Heat Capacity

The effect of vacuum annealing on the heat capacity of niobium is somewhat ambiguous. From Fig. 4 it is evident that the heat capacities in the superconducting state for Nb I, II, and III are identical within experimental error. However, the heat capacity in the normal state appears to be somewhat greater for Nb I than for Nb II in the temperature range 7 to 9°K. In this temperature range, the data for Nb I are similar to those of Brown *et al.*[3] on what was probably a similar but untreated sample. If the effect of annealing is to improve the purity of the sample as well as decrease the hardness, one might expect the heat capacity to increase with successive annealing due to a decrease in the Debye θ. This is evident in the heat capacity of vanadium reported by Worley, Zemansky, and Boorse.[14] On the other hand, the heat capacity may decrease due to a decrease in the electronic specific heat as shown in the case of tantalum by the above authors. Since the samples Nb II and III were the best annealed and purified material used in the research, the heat capacities of these samples are used in the calculation of the thermodynamic properties given below.

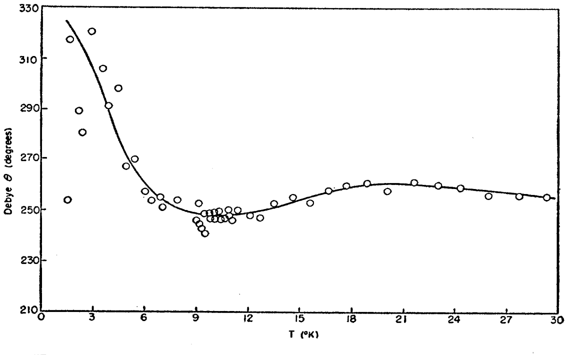

FIG. 6. Debye θ as a function of temperature of Nb II.

The heat capacity of a superconductor in the normal state, C_n, at low temperatures can be expressed by the Debye-Sommerfeld relation as the sum of an electronic term and lattice term:

$$C_n=\gamma T+464.4(T/\theta)^3.$$

TABLE V. Critical field as a function of temperature.

T (°K)	$\Delta S\times10^4$ e.u.	H_c (gauss)
0	0.0	1944
1	18.80	1920
2	36.80	1848
3	52.65	1726
4	63.30	1554
5	66.90	1335
6	63.20	1072
7	52.00	767
8	32.25	423
9	4.55	63
9.17	0.0	0

If, in the temperature range in which the heat capacities are determined, the Debye θ remains constant, then γ can readily be evaluated from a plot of C_n/T *versus* T^2. Examination of Fig. 5 shows that this plot does not lead to a straight line in the experimental temperature range 1.5 to 30°K. Thus the Debye θ is not constant for niobium. This is consistant with the theoretical calculations of the heat capacity from the normal modes of vibration for a body-centered cubic lattice by Fine.[15] His results, based on the measured elastic constants of a single crystal of tungsten, indicate that the Debye θ for this metal starts from a value of 367 degrees at the absolute zero and falls monotonically with increasing temperature to a constant value of approximately 300 degrees at 55°K. Although the values of the Debye θ for tungsten deduced from the heat capacity data of Horowitz and Daunt[16] are in considerable disagreement with the calculations of Fine, they nevertheless show an even stronger dependence of the Debye θ with temperature. Since it is impossible to evaluate independ-

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[14] Worley, Zemansky, and Boorse, Phys. Rev. **99**, 447 (1953).

[15] P. C. Fine, Phys. Rev. **56**, 355 (1939).

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

ently the variation of the Debye θ with temperature for niobium, the value of the electronic specific heat term γ cannot be simply evaluated from the heat capacity data. Choosing a value for γ of $(18.0\pm1.0)\times10^{-4}$ cal mole^{-1} deg^{-2}, reasonable curves for the variation of the Debye θ with temperature are obtained. If $\gamma=19.0\times10^{-4}$, the Debye θ decreases from a value of approximately 330 degrees at the lowest temperature to a constant value of 258 degrees at higher temperatures. This is shown in Fig. 6. If a value of 17.0×10^{-4} is chosen, the variation of the Debye θ with temperature is very similar to that of Horowitz and Daunt[16] for tungsten, with a maximum occurring at approximately 5°K ($\theta=252$). The value of γ reported by Brown, Zemansky, and Boorse[3] is 20.4×10^{-4} cal mole^{-1} deg^{-2}.

An attempt was made to fit the heat capacity of niobium in the superconducting state, C_s, to an empirical relation of the form

$$C_s=AT^n,$$

where A and n are constants. Large deviations occurred at the lowest temperatures.

2. Calculation of the Critical Field of Niobium from the Heat Capacity Data

The critical magnetic field H_c as a function of temperature can be deduced from the heat capacity by using the following expression:

$$\Delta C=C_n=C_s=-\frac{VT}{4\pi}\frac{d}{dT}\left(H_c\frac{dH_c}{dT}\right),$$

where V is the molar volume at temperature T. Integrating the expression twice, first from 0°K to T and then from T to T_c, the zero field transition temperature, one obtains

$$H_c^2=\frac{-8\pi}{V}\int_T^{T_c}\left\{\int_0^T\left(\frac{C_n-C_s}{T}\right)dT\right\}dT,$$

where the term in the curly brackets corresponds to the difference in entropy between the normal and superconducting states. The critical-field data for niobium, as well as the difference in entropy between the normal and superconducting states, are given in Table V as a function of temperature. The molar volume of niobium was estimated to be 10.80 cc mole^{-1} from 0 to 10°K on the basis of the thermal-expansion data of Edwards, Speiser, and Johnston.[17] The critical-field data are plotted in Fig. 7 *versus* the square of the temperature. The curve deviates somewhat from a straight line indicating that the critical field is not given by the simple parabolic relationship. The initial slope of the critical field $(dH_c/dT)_{T=T_c}$ and the critical field at absolute zero, H_0, are -415 ± 2 gauss deg^{-1} and 1944 ± 10 gauss, respectively. The initial slope calculated from Rutger's equation,

$$\Delta C_{T=T_c}=0.0335=\frac{-VT_c}{4\pi}\left[\left(\frac{dH_c}{dT}\right)^2\right]_{T=T_c},$$

gives a value of 421 ± 4 gauss deg^{-1}. The large uncertainty here is due to the uncertainty in the extrapolation of the heat capacity of niobium in the superconducting state to the transition temperature. The values of $(dH_c/dT)_{T=T_c}$ and H_0 reported by Brown, Zemansky, and Boorse from their calorimetric data are -453 gauss deg^{-1} and 2000 gauss, respectively.

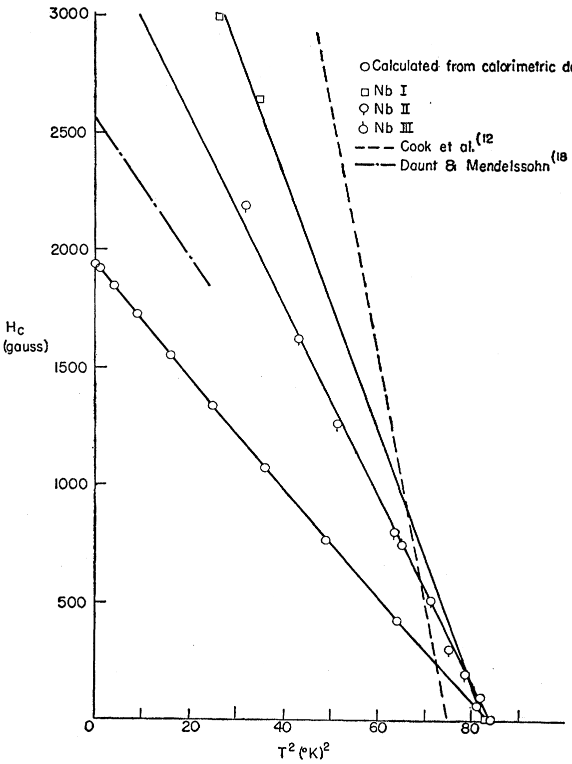

FIG. 7. Critical field of Nb.

3. Effect of Annealing on the Zero-Field Transition Temperature and Critical Field. Comparison with Calorimetric Data

The effects of annealing on the magnetic properties of niobium and the zero-field transition temperature are clearly demonstrated in Fig. 7, and in Table VI. Cook, Zemansky, and Boorse[12] annealed their sample at 1000°C for five hours. Since it is probable that their Fansteel niobium sample was similar to the one used in this research, their results[18] are included in Table VI.

It is clear from Table VI that vacuum annealing did not reduce the Nb sample to a so-called ideal superconductor and that further treatment even at 2100°C

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[17] Edwards, Speiser, and Johnston, J. Appl. Phys. **22**, 424 (1951).

[18] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).

TABLE VI. Effect of vacuum annealing on the magnetic properties of niobium.

	Annealing temperature (°C)	T_c (°K)	$\left(\frac{\partial H}{\partial T}\right)_{T-T_c}$ gauss deg^{-1}	H_0 (gauss)
	1000 (5 hr)	8.65	−1910	8250[a]
(Nb I)	1200–1600 (8 hr)	9.07	−1148[b]	4760[b]
(Nb II)	1450–2100 (20 hr)	9.17	− 734[b]	3370[b]
(Nb III)	2100 (8 hr)	9.17	− 734[b]	3370[b]
	Calorimetric data	9.17	− 415	1944

[a] See reference 12.

[b] These values were calculated on the assumption that the parabolic relation for the critical field is valid.

leads to no visible improvement. This was not the case in tantalum[19] where vacuum annealing produced an ideal superconductor. The reason for the difference in behavior between niobium and tantalum may be in the fact that a substantial amount of tantalum is present in the niobium sample. This cannot be removed by vacuum annealing and may result in internal stresses. The magnetic behavior of niobium may be considered comparable to some alloys (even soft superconducting alloys) which exhibit unusually large critical fields.[20]

4. Comparison of the Heat Capacity with Two-Fluid Models of Superconductivity

The experimental heat-capacity data were compared with the theoretical relations of Marcus and Maxwell[21] and Koppe[2,22] based on the two-fluid model. In both cases $C_{\mathrm{el}}/\gamma T$ is expressed as a function of T/T_c where C_{el} is the electronic contribution to the heat capacity in the superconducting state. In order to make the comparison, the generally accepted assumption that the heat capacity in the superconducting state is the sum of two terms, lattice and electronic, must be employed in conjunction with the data. C_{el} is obtained by subtracting the lattice term from the total heat capacity in the superconducting state, C_s. Since the Debye θ is not a constant for niobium in the temperature range of interest. C_{el} was evaluated from the experimental data by using the relationship

$$C_{\mathrm{el}}=C_s-C_n+\gamma T.$$

The choice of γ is important if a positive value for C_{el} at the lowest temperatures is to be obtained. For this reason $\gamma=19.0\times10^{-4}$ cal mole^{-1} deg^{-2} was chosen, even though the more probable value, reported earlier in this discussion, was $(18.0\pm1.0)\times10^{-4}$ cal mole^{-1} deg^{-2}. Comparison of the $C_{\mathrm{el}}/\gamma T$ so calculated with that obtained from the Marcus and Maxwell relationship, for any value of α, the undetermined constant in their equation, gives relatively poor agreement. Agreement with the Koppe relation, however, is remarkably good in the range $T/T_c=0.25$ to 1.0. Below $T/T_c=0.25$, the deviations are as large as 300% at the lowest temperature.

Corak, Goodman, Satterwaite, and Wexler[23] have shown that C_{el} for superconductors could be represented, below approximately $0.7T_c$, by an empirical exponential relation of the form

$$C_{\mathrm{el}}/(\gamma T_c)=AC^{-bT_c/T}.$$

As in the case of Koppe's theory, this relationship agrees with the experimental data only at the higher values of T/T_c.

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[19] White, Chou, and Johnston, Phys. Rev. **109**, 797 (1958), following paper.

[20] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), p. 42.

[21] P. M. Marcus and E. Maxwell, Phys. Rev. **91**, 1035 (1953).

[22] H. Koppe, Ann. Physik **1**, 405 (1947).

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