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The Superconducting and Normal Heat Capacities of Niobium*

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Data on the heat capacity of niobium in the normal and superconducting phases are presented in the temperature interval 2.5°K to 11°K. The normal heat capacity c_n was found to be given by the usual relation: $c_n=\gamma T+464T^3/\Theta^3$, where $\gamma=20.4\times10^{-4}$ cal/M deg^2 and $\Theta=252$°K. The zero-field transition temperature T_0 was found to be 8.70°K±0.10°, and the heat capacity discontinuity Δc at this temperature to be 0.0368 cal/M deg. The heat capacity in the superconducting phase was found to depart from a T^3 dependence below 5°K. The entire curve could not be represented by either the Koppe relation or the α model. The H_T *vs* T curve deduced from the heat capacity data was found to be very nearly parabolic, with the value of $H_0=2000$ gauss and dH_T/dT at the zero-field transition temperature equal to 453 gauss/deg.

I. INTRODUCTION

When a pure superconducting element undergoes a reversible isothermal transition from the superconducting phase s to the normal phase n at temperature T and magnetic field H_T, the change in the molar heat capacity c is given by

$$c_n-c_s=-\frac{vT}{4\pi}\frac{d}{dT}\left(H_T\frac{dH_T}{dT}\right). \tag{1}$$

Although there have been direct calorimetric determinations of c_n and c_s for several of the soft superconductors and for a few of the hard superconductors, much of the heat capacity data listed in the literature has been calculated with the aid of Eq. (1) from the experimental determinations of the relation between H_T and T (the so-called H_T *vs* T curves).

The recent discovery of the isotope effect among superconducting isotopes has stimulated very accurate measurements of the H_T *vs* T curves. In the case of the soft superconductors, various investigations on different samples of any given element have yielded substantially the same results, whereas in the case of the hard superconductors this has not been true. The following reasons may be given: (1) different samples of a hard superconductor vary in purity and internal stress, to which the magnetic behavior seems to be very sensitive; (2) the magnetic field necessary to destroy superconductivity at a given temperature depends on the method used to detect the onset and completion of the phase transition. In the case of niobium, whose zero-field transition temperature has been variously reported between 5°K and 9.6°K,[1-6] the H_T *vs* T curves were measured in only three of these investigations[3,5,6] and serious disagreement was found among them. Since no reliable heat capacity data can be inferred from them, direct calorimetric determinations of c_n and c_s were therefore desirable.

Many measurements of the heat capacity of pure elements (mostly nonsuperconductors) have been made in recent years, the principal object being to examine the validity of the Debye-Sommerfeld relation which expresses the molar heat capacity as the sum of a term linear in T attributable to the free electrons, and a T^3 term arising from the lattice, *viz.*,

$$c_n=\gamma T+(464/\Theta^3)T^3. \tag{2}$$

This formulation has recieved ample confirmation from many experimental studies on nonsuperconducting elements. In addition the experimental results thus far available support the fact that the behavior of the superconducting elements *when maintained in the normal phase* by a suitable magnetic field also follows the relation expressed by Eq. (2).

Until recently, direct calorimetric measurements of the heat capacity *in the superconducting phase* were were interpreted to indicate a T^3 dependence, as though a superconductor had only a lattice heat capacity. Application of the Debye T^3 equation in conjunction with these measurements yielded values of a Debye Θ smaller than that appropriate to the normal phase. A T^3 dependence of the heat capacity in the superconducting phase can be derived from Eqs. (1) and (2) provided a parabolic relation between H_T and T is assumed. Since many of the measured H_T *vs* T curves are nearly parabolic, there seemed to be a satisfactory consistency between magnetic and calorimetric properties in the superconducting phase, although the low values of the Debye Θ had no theoretical significance whatever. In recent years, however, much more careful measurements of the H_T *vs* T curves and of superconducting heat capacities have been made, with the result that both the parabolic law and the T^3 dependence in the superconducting phase have turned out to be only approximations.

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[1] W. Meissner and H. Franz, Z. Physik **63**, 558 (1930).

[2] Meissner, Franz, and Westerhoff, Ann. Physik **17**, 593 (1933).

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

[4] Ziegler, Bruksch, and Hickman, Phys. Rev. **62**, 554 (1942).

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

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

A recent theory due to Koppe[7] postulates that the lattice heat capacity in the superconducting phase is identical with that in the normal phase. The remainder of the heat capacity arises from the electrons and is expressible as a function of the reduced temperature T/T_0, this function being the same for all superconductors. This theory can be tested most favorably using an element which (1) has a large Debye characteristic temperature, since in this case the heat capacity will be primarily due to the electrons, and which (2) possesses a high transition temperature T_0 since this circumstance makes experimentally available a wider range of reduced temperatures without resorting to the adiabatic demagnetization technique.

These criteria are best fulfilled by the metals niobium, vanadium, and tantalum.[8] This paper presents heat capacity data for the first metal of this group, niobium, in both the normal and superconducting phases. The related study on vanadium and tantalum is now in progress, preliminary data having already been reported for vanadium.[9] The present measurements were made on a single sample of niobium supplied by the Fansteel Metallurgical Corporation, and specified as annealed, strain-free, and of the purest grade available. Previous experience in this laboratory[5] with Fansteel niobium indicates a purity of 99.8 percent.

II. EXPERIMENTAL METHOD

The calorimeter used in these determinations is shown in Fig. 1. A cylindrical specimen of niobium of diameter 1.26 cm, height 4.75 cm, mass 50.76 g (0.55 mole) was suspended by a fine Nylon thread in the experimental space S. A carbon resistance thermometer was mounted in a transverse hole through the center of the specimen. Heat could be supplied electrically by means of a coil of constantan wire (No. 40 B&S gauge) wound noninductively around the outside of the specimen. The heater wire was thermally bonded to and electrically insulated from the niobium by means of several layers of clear Glyptal lacquer each about 0.5 mil thick. Each layer was thoroughly baked before the next was applied. The thermometer and heater leads each consisting of about a meter of No. 40 B&S gauge enameled copper wire were led from the specimen to a Stupakoff seal B. Connections to the other side of the seal were brought down into the helium bath and then out of the cryostat. The experimental space S could be evacuated through a one-inch tube which had an offset in the helium bath to insure that all radiation to the specimen came from surfaces at helium temperatures. The liquid helium container C (capacity 1.5 liters) was equipped with a 0.5-inch diameter tube for pumping on the helium bath, and a 0.125-inch diameter tube which extended below the surface of the liquid helium, the function of which was to measure the vapor pressure. The liquid helium bath was separated from the liquid nitrogen space E by a highly evacuated space D.

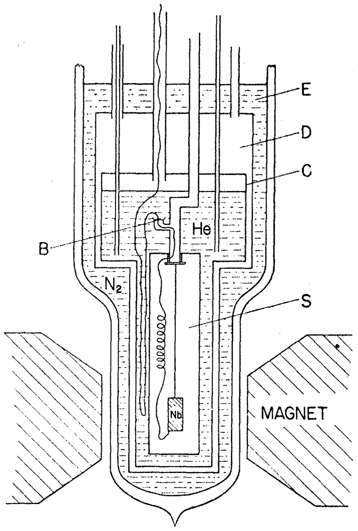

FIG. 1. Simplified schematic diagram of the adiabatic calorimeter.

The thermometer consisted of an Allen-Bradley carbon composition radio resistor rated at 0.5 watt and 56 ohms at room temperature. It was prepared and mounted as described by us in a previous publication in this journal.[10] The thermometer was calibrated in the liquid helium range (2°–4.2°K) and in the liquid hydrogen range (14°–20°K). A total of ninety calibration points was taken in the course of eight runs extending over a period of five months (June through October 1951). It was found that the data could be represented with high accuracy by a modification of the semiconductor equation in the form

$$\log R = A + BT^{-1} + CT^{-2} - KT^2,$$

where, for this particular resistor, $A = 1.90554$, $B = 5.22291$, $C = 12.14932$, and $K = 0.000068$. A few typical values are given in Table I. The agreement between experimental calibration points and the empiric equation was such that over 90 percent of the points in the helium range differed by less than 0.002° from the equation.

The molar heat capacity c is given by the equation

$$c = \frac{1}{n} \cdot \frac{dQ}{dT} = \frac{1}{Jn} \cdot \frac{(i_H)^2 R_H \Delta\tau}{\Delta T},$$

where n is the number of moles, J is the mechanical equivalent of heat, i_H is the heater current, R_H is the heater resistance, $\Delta\tau$ is the time interval during which i_H is applied, and ΔT is the temperature change brought about by the electrical energy input. The mass of the thermometer, Glyptal, and heater amounted to only 0.9 percent of the mass of the niobium. Corrections for the heat capacity of these parts of the system were used

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

[8] P. L. Bender and C. J. Gorter, Physica **18**, 597 (1952).

[9] Worley, Zemansky, and Boorse, Phys. Rev. **87**, 1142 (1952).

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TABLE I. Typical thermometer calibration and sensitivity.

T, °K	R, ohms	dR/dT, ohms/deg K
Room temperature	56	...
20	136.2	4.941
14	179.6	11.16
9	284.3	39.15
4.2	1061.8	583.4
3	2553	2478
2	9537	16 880

to provide an effective value for n which was estimated to be in error by no more than 0.25 percent. The magnitude of i_H was computed from the potential difference across a 10-ohm Wolff standard resistance in series with the heater. This potential difference was measured during each of the individual heat capacity determinations by means of a Leeds and Northrup Type K potentiometer. The potential difference across the heater itself was also measured with a Leeds and Northrup Type K potentiometer, and R_H was found to be constant at the value 96.9 ohms within 0.1 percent over the range of temperature in which heat capacity measurements were made. The time interval $\Delta\tau$ was measured by a standard electric timer which could be read to the nearest 0.01 second. The same switch that controlled the heater current also controlled the electric timer so that the period during which heater current was supplied was known to a few hundredths of a second. The percentage error introduced by this uncertainty was of the order of 0.1 percent, which, as will appear, is not significant.

The temperature interval ΔT was determined as follows. The current through the resistance thermometer was kept constant at 10 microamperes by reading the potential difference across a 100-ohm Wolff standard resistance in series with the thermometer. Separate potential leads were brought out of the cryostat from the Stupakoff seal B to a Leeds and Northrup Wenner potentiometer which was used to measure the potential difference across the thermometer. The resistance of the thermometer was measured at intervals of approximately ten seconds for about one minute both before and after energy was supplied to the heater. A typical plot of resistance *vs* time is shown in Fig. 2. Such a graph was made for each of the heat capacity determinations. In most of these, the fore and after period plots were linear or only very slightly curved. Measurements made during the heating period showed a linear resistance variation with time as indicated in the figure. The fore and after period curves were extrapolated to the center of the heating interval $\Delta\tau$. The graph was then used to determine R_{Av} and ΔR. When the method Keesom and Kok[11] was used to analyze some typical curves the result in every case was identical with that obtained by measuring ΔR at the center of the heating interval as shown. The temperature appropriate to a determination of the heat capacity was obtained from R_{Av} and the calibration curve. The temperature interval ΔT was determined from the relation

$$\Delta T = \Delta R/(dR/dT),$$

where dR/dT was computed (at the temperature corresponding to R_{Av}) from the empirical relation, Eq. (3), for the thermometer calibration curve. In order to present a more detailed picure of the experimental data entering into the evaluation of the heat capacity, the raw data appropriate to eleven typical points are listed in Table II.

To measure the heat capacity in the normal state at temperatures below T_0, a constant transverse magnetic field of approximately 5000 oersteds was applied to the specimen by means of an electromagnet. This field was found to be sufficient to maintain the niobium in the normal state down to the lowest temperatures. Although it was recognized that a larger sample would yield better data, the 0.55-mole specimen was the largest size that could be used in view of the limited space over which the field was uniform.

With the exception of the quantity ΔT, the error in the measurement of each of the quantities needed to compute the heat capacity is of the order of 0.1 percent or smaller. The error in ΔT depends on the accuracy with which ΔR can be derived from the graphs of the type shown in Fig. 2. Since the resistance thermometer has greater sensitivity below 5°K, the value of ΔR and thus ΔT in this range could be determined to 3 percent or better in almost every case. Data above 5°K show a greater scatter.

III. EXPERIMENTAL RESULTS

The normal and superconducting molar heat capacities of the niobium specimen are plotted against temperature in Fig. 3. The curves are constructed from over 220 separate heat capacity determinations, each calculated from data obtained from a graph similar to that in Fig. 2. The value of T_0 at which the discon-

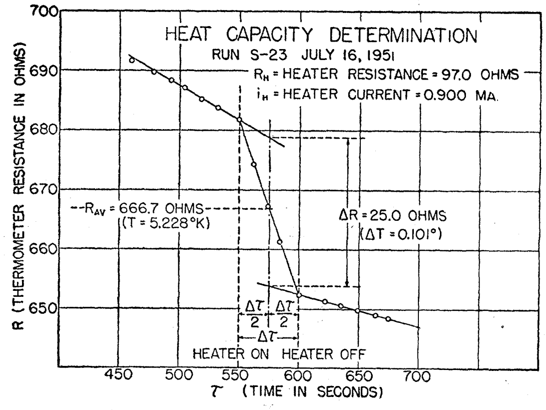

FIG. 2. Typical heating curve with fore and after periods.

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[11] W. H. Keesom and J. A. Kok, Leiden Comm. No. 219 c, reprinted from Proc. Koninkl. Akad. Wetenschap. Amsterdam **35**, 294 (1932).

TABLE II. Raw data for eleven typical heat capacity determinations.

Run number	Magnet	R ohms	T °K	ΔR ohms	dR/dT ohms/deg	ΔT deg	$\Delta\tau$ sec	i_H ma	C_v $\frac{\text{cal}}{\text{M deg}}$
S-133	off	4130	2.563	204	5180	0.0394	27.29	0.200	0.001168
S-136	off	2303	3.110	83.5	2095	0.03986	57.07	0.200	0.002414
S-144	off	1015.6	4.282	18.7	549.5	0.03403	27.52	0.500	0.008520
S-194	off	837.2	4.675	13.1	380.7	0.03441	34.81	0.500	0.01066
S-23	off	666.6	5.228	25.3	249	0.1016	50.00	0.900	0.01680
S-29	off	368	7.42	7.55	72.3	0.1072	50.00	1.500	0.04424
N-88	on	2066	3.233	26.8	1768	0.01516	40.00	0.25	0.006951
N-97	on	1193.8	3.996	42.1	715	0.05888	40.00	0.600	0.01031
N-64	on	496.8	6.144	18.3	138.2	0.1324	60.00	1.000	0.01910
N-69	on	299.8	8.63	5.65	44.62	0.1266	50.00	1.500	0.03746
S-120	off	238.5	10.475	3.40	24.87	0.1367	40.00	2.100	0.05439
				(R_H=96.9 ohms, $1/Jn$=0.435)					

tinuity in the heat capacity occurs was found to be 8.70°K±0.10° by a careful analysis of the ΔT values associated with the individual points in the transition region. This is in agreement with the value found previously by another method in this laboratory.[5]

Expressing the heat capacity in the normal phase, at low temperatures, as the sum of an electronic term and a lattice term, as given by Eq. (2),

$$c_n = \gamma T + (464/\Theta^3)T^3,$$

the values of γ and Θ may be conveniently found by plotting c_n/T *vs* T^2. Such a graph for values of T up to 10°K is shown in Fig. 4. It is seen, as would be expected, that the points immediately above T_0 both with and without a magnetic field lie on the same straight line as those with a field below T_0. Extrapolation of this straight line yields a value of γ equal to 20.4×10^{-4} cal/M deg^2. The slope of this straight line yields a value for the Debye Θ equal to 252°K. Measurements of the heat capacity were made up to 20°K and a plot of these data was published previously in this journal.[12] Inspection of this plot shows that, above 12°K, the experimental points fall below the straight line, indicating an increase in Θ in this temperature range.

According to present theoretical ideas, the molar heat capacity *in the superconducting phase* is also considered to be the sum of two terms, one due to the lattice vibrations represented by the *usual* Debye T^3 term with the *normal* Debye Θ, and a remainder attributed to the electrons. This electronic contribution, denoted by c_s^{el}, is therefore obtained by subtracting the lattice term from the measured superconducting heat capacity. For comparison with the current theories

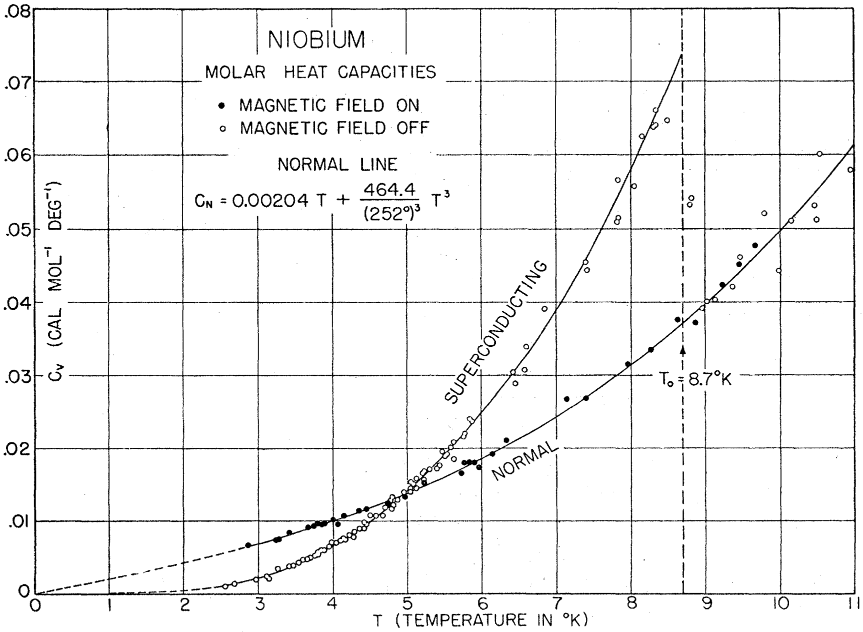

FIG. 3. Temperature dependence of the heat capacities of niobium.

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[12] Brown, Zemansky, and Boorse, Phys. Rev. **86**, 134 (1952). The values of γ and Θ reported in this reference were preliminary and are superceded by those in the present paper.

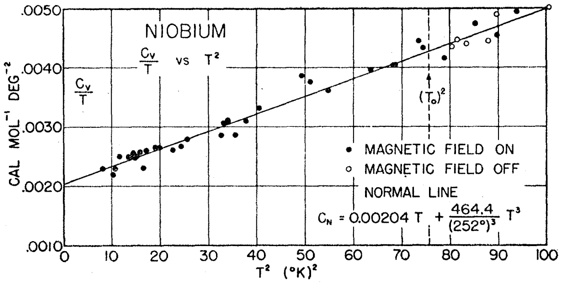

FIG. 4. c/T vs T^2 plot of the heat capacity of niobium in the normal phase.

discussed in the following section, the variation in c_s^{el} with temperature is most conventiently represented by plotting $c_s^{\mathrm{el}}/\gamma T$ against the reduced temperature T/T_0.

The plot using these coordinates is shown in Fig. 5 and was obtained in the following way. A smooth curve was drawn through all the points appropriate to the superconducting phase. At half-degree intervals, the value of the T^3 term in Eq. (2) was subtracted from the value of the superconducting heat capacity as determined from the smooth curve. These differences were then divided by the appropriate values of γT. Table III lists the numerical values involved.

IV. DISCUSSION

The numerical values obtained experimentally for the heat capacities may be utilized in two ways: (1) to calculate the H_T vs T curve appropriate to a sample of niobium which is capable of undergoing reversible magnetic transitions between the normal and superconducting phases, and (2) to test the predictions of theories of superconductivity.

A. Calculation of the H_T vs T Curve

If a superconducting element undergoes a reversible transition between the normal and superconducting phases at any temperature T and magnetic field H_T, the difference of the heat capacities is given by Eq. (1), namely,

$$\Delta c = c_n - c_s = -\frac{vT}{4\pi}\frac{d}{dT}\left(H_T\frac{dH_T}{dT}\right). \tag{5}$$

At $T=T_0$ this reduces to Rutger's equation,

$$(\Delta c)_{T=T_0} = -\frac{vT_0}{4\pi}\left(\frac{dH_T}{dT}\right)^2_{T=T_0}, \tag{6}$$

which may be used to compute $(dH_T/dT)_{T=T_0}$. For the sample of niobium used in this experiment $(\Delta c)_{T=T_0}$ equals 0.0368 cal/M deg and T_0 equals 8.70°K, whence $(dH_T/dT)_{T=T_0}$ equals 453 gauss/deg.

Integrating Eq. (1) between 0°K and T, we get

$$\int_0^T \frac{c_n-c_s}{T}dT = -\frac{v}{4\pi}H_T\frac{dH_T}{dT}. \tag{7}$$

In order to evaluate the left-hand member, c_n/T and c_s/T were plotted against T. The plot for c_s/T was extrapolated to zero at absolute zero by means of a smooth curve. The uncertainty introduced by this extrapolation was found to be negligible because the area under this extrapolated portion is such a small fraction of the area under the c_n/T curve in this temperature range. It can be seen from Eq. (7) that when T is equal to T_0, H_T is zero, thus the left-hand member vanishes. A plot of the left-hand member (which is the entropy difference) against T rises from zero at absolute zero to a maximum, and then descends sharply, cutting the temperature axis at T_0. This provides a sensitive means for determining the zero-field transition temperature T_0. The value of T_0 obtained in this way was found to be 8.70°K (in exact agreement with the value found in the preceding section by analyzing the zero-field experimental points in the neighborhood of T_0). There is very little leeway in determining T_0 in this manner since the sharp intersection point is determined by the shapes of the c_n/T and c_s/T curves throughout their entire range. Changes in the shapes of these curves within the limits of experimental error would produce a change in T_0 of only a few hundredths of a degree.

A second integration of Eq. (7) from T to T_0 yields

$$\int_T^{T_0}\left[\int_0^T \frac{c_n-c_s}{T}dT\right]dT = -\frac{v}{4\pi}\frac{(H_T)^2}{2}, \tag{8}$$

from which it is possible to compute H_T for all values of T from 0°K up to T_0. This integration was performed graphically by planimeter using a plot of

$$\int_0^T [(c_n-c_s)/T]dT$$

vs T. The data computed in this manner were used to construct a plot of H_T vs T^2, which is shown in Fig. 6. The critical magnetic field H_0 necessary to destroy superconductivity at absolute zero was found to be 2000 gauss. The points plotted in Fig. 6 are very close to the straight line, so that the H_T-T curve is approxi-

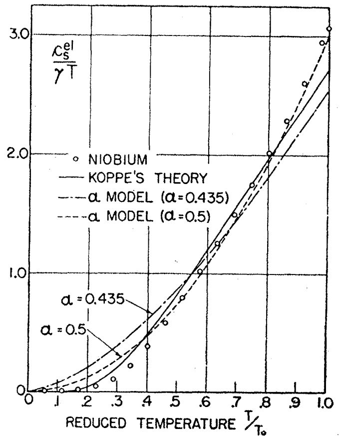

FIG. 5. Ratio of the superconducting to the normal electronic heat capacity of niobium vs reduced temperature. Circles represent experimental points; solid curve, Koppe's theory; dashed curves, α model.

mately parabolic. A rigorously parabolic curve would have been obtained if c_s had been strictly proportional to T^3. The departure from T^3 dependance exhibited by the experimental c_s results is clearly beyond the limit of experimental error, as shown in a previous publication.[12] This departure is still not large enough to give rise to an H_T-T curve that differs appreciably from a parabola.

B. Tests of Theories of Superconductivity

On the basis of Heisenberg's theory[13] of superconductivity, Koppe[7] calculated the ratio of the superconducting electronic heat capacity c_s^{el} to the normal electronic heat capacity γT to be a universal function of the reduced temperature T/T_0, thus

$$\frac{c_s^{\mathrm{el}}}{\gamma T}=\frac{f(T/T_0)}{T/T_0}.$$

The right-hand member was recalculated for various reduced temperatures by R. D. Worley of this laboratory, and the results are listed in the last column of Table III. The value $c_s^{\mathrm{el}}/\gamma T$ as determined from Kopp's theory is plotted against T/T_0 as the solid curve in Fig. 5. It is seen that the experimental points do not agree with Koppe's theory. Similar graphs of the experimental results on tin and indium, and of tentative data on vanadium and tantalum[9] also indicate a rough agreement with the shape of Koppe's curve, but no real agreement in detail. It may be concluded that experimental measurements of c_s^{el} do not support the contention that $c_s^{\mathrm{el}}/\gamma T$ is a universal function of T/T_0. In other words, it may be suspected that Koppe's theory, although qualitatively correct, is too inflexible and might be made to agree more closely with experiment by introducing an adjustable parameter, different for each superconductor.

TABLE III. Smoothed data giving the ratio of the superconducting to the normal electronic heat capacity of niobium.

T°K	C_s cal/M deg	C(lattice) cal/M deg	C_s^{el} cal/M deg	T/T_0 (T_0=8.70°K)	$C_s^{\mathrm{el}}/\gamma T$	$C_s^{\mathrm{el}}/\gamma T$ (Koppe's theory)
0	0	0	0	0	0	0
0.5	[0.00001][a]	0.000004	0.000006	0.058	0.0059	0
1.0	[0.00005]	0.00003	0.00002	0.115	0.0098	0.0012
1.5	[0.00017]	0.00010	0.00007	0.172	0.0229	0.016
2.0	[0.00044]	0.00023	0.00021	0.230	0.0512	0.078
2.5	0.00103	0.00046	0.00057	0.288	0.1118	0.184
3.0	0.00216	0.00079	0.00137	0.345	0.2239	0.330
3.5	0.00403	0.00125	0.00278	0.402	0.389	0.500
4.0	0.00668	0.00187	0.00481	0.460	0.589	0.700
4.5	0.01004	0.00266	0.00738	0.517	0.804	0.905
5.0	0.01410	0.00365	0.01045	0.575	1.024	1.12
5.5	0.0190	0.00486	0.0141	0.632	1.257	1.32
6.0	0.0247	0.00631	0.0184	0.690	1.496	1.54
6.5	0.0313	0.00802	0.0233	0.747	1.753	1.76
7.0	0.0389	0.01001	0.0288	0.805	2.02	1.99
7.5	0.0475	0.01232	0.0352	0.862	2.29	2.21
8.0	0.0576	0.01495	0.0427	0.919	2.61	2.42
8.5	0.0690	0.01793	0.0511	0.977	2.95	2.63
8.7 (T_0)	0.0738	0.01923	0.0546	1.000	3.07	2.71

[a] Brackets indicate extrapolated values.

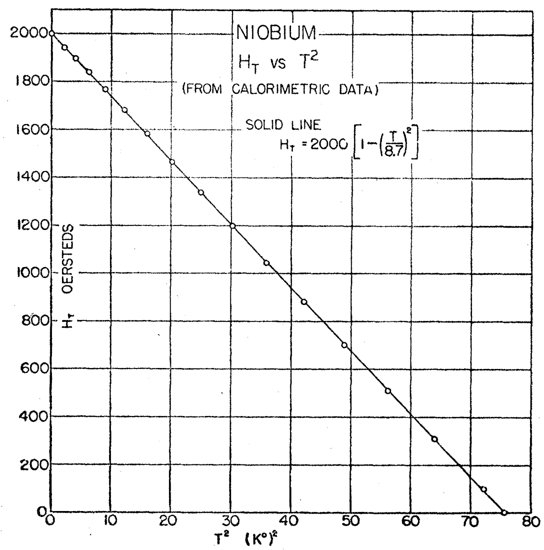

FIG. 6. H_T vs T^2 curve for niobium calculated from calorimetric data.

In an attempt to explain the slight departure from the parabolic relation between the critical magnetic field and temperature displayed by the precise experimental measurements of Maxwell on tin, thallium, and indium, Marcus and Maxwell[14] have recently extended the two-fluid theory of Gorter and Casimir.[15] According to this theory, the electrons in a superconducting metal are assumed to undergo a sort of condensation below the transition temperature T_0. The fraction ω of the electrons that are in the superconducting state is assumed to be a function of T/T_0. The number of normal electrons $K(\omega)$ was assumed by Gorter and Casimir to depend on ω according to

$$K(\omega)=(1-\omega)^{\frac{1}{2}}.$$

On this assumption it was possible to derive the parabolic law for the threshold field curve and with it a T^3 dependence of c_s^{el}. Marcus and Maxwell made the assumption that

$$K(\omega)=(1-\omega)^{\alpha},$$

where α is a constant less than $\frac{1}{2}$ and different for different elements. It was found that the resulting form of the threshold field curves agreed well with Maxwell's experiments when values of α were chosen between 0.50 and 0.38. On the basis of this "α" model, it was found

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[13] W. Heisenberg, Z. Naturforsch. **2a**, 185 (1947); Ann. Physik **3**, 289 (1948).

[14] P. M. Marcus and E. Maxwell, National Bureau of Standards Report 2496 (unpublished).

[15] C. J. Gorter and H. Casimir, Physik. Z. **35**, 963 (1934).

that

$$\frac{c_s^{\mathrm{el}}}{\gamma T}=\frac{1+\alpha}{1-\alpha}(T/T_0)^{2\alpha/(1-\alpha)}.$$

The dashed curves in Fig. 5 are plots of this equation for two different values of α. It may be seen that the niobium data do not fit any of the α curves, so that it may be concluded that there is as yet no theory of the heat capacity of superconductors which is in satisfactory agreement with these experiments.

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The Vibrational Spectrum and Specific Heat of Sodium

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The frequency spectrum of the normal vibrations of a body-centered cubic crystal lattice is derived by a method suggested by Houston, in which the secular equation is solved along three lines in the reciprocal lattice and the result is interpolated by means of suitably chosen spherical harmonics. Some corrections are applied to the high-frequency part of the spectrum, and the lattice part of the specific heat of metallic sodium is calculated as a function of temperature.

I. THE PROBLEM

In the theory of ideal metals one considers effectively free conduction electrons moving in the field of a lattice of positive ions. These conduction electrons move very fast compared with the ions of the lattice, and are relatively weakly coupled to them, so that an "adiabatic" separation is always made as follows. In considering properties of the conduction electrons one regards the ions as at rest or at most vibrating as a perturbation (to give the thermal part of the resistivity); conversely, in the study of lattice properties such as the specific heat at intermediate temperatures and a large part of the elastic constants, the lattice is regarded as held together by the "smeared-out" field of the electrons.

Here we are interested in calculating the specific heat of metallic sodium at moderately low temperatures, i.e., between about 10°K and 100°K, and in this region the only effective contribution comes from the lattice of ions. At extremely low temperatures, the electronic contribution to the specific heat becomes important, while at high temperatures the specific heat has approximately the value predicted by classical equipartition, but with some disturbing effects believed to be due to the large amplitude of the lattice vibrations and consequent anharmonicity and also due to the electrons. There is an additional disturbing effect in the case of sodium giving a peak in the specific heat at about 7°K.[1] Such effects are known to occur in a number of the crystal. Then, to get physical results, we apply substances: they may arise because of changes in crystal structure, but in any case they cannot be accounted for in terms of lattice vibrations.

To calculate the specific heat we just have a statistical knowledge of the degrees of freedom of the ions. For this purpose it is convenient to regard the ions as making up a lattice and to study the frequency spectrum of the lattice vibrations, which are the normal modes of the system. The reason for doing this statistically is that in a macroscopic crystal there are $\sim 10^{23}$ ions, i.e. $\sim 3\times 10^{23}$ degrees of freedom.

The best method that has been developed so far for obtaining the frequency spectrum is that of Born and v. Karman,[2] who set up the classical equations of motion of an ion interacting with its close neighbors, with given force constants as parameters. These parameters are to be determined from the elastic constants of the lattice. With the use of Born's cyclic boundary conditions, the condition that the equations of motion have a nonvanishing solution corresponding to small harmonic vibrations of the ions about their equilibrium positions gives the secular equations. Thus, if there are N atoms in a three-dimensional lattice, there are N distinct 3×3 secular determinants in the simplest case; these have $3N$ roots, the frequencies of the normal modes of vibration. We are interested in finding the frequency spectrum of these $3N$ vibrations, i.e., finding how many of them lie in any given frequency range. This frequency distribution is obtained by solving a suitable number of the $N(\sim 10^{23})$ secular equations.

Thus we obtain a frequency spectrum by setting up classical equations of motion in terms of certain force constants which are related to the elastic properties of

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