TABLE I. Lattice constants of MnBi (NiAs structure).

	Room-temperature phase	High-temperature phase
Present data	c—6.118 A a—4.287 A	c—5.964 A a—4.339 A
Guillaud's data	c—6.12 A a—4.30 A	c—5.83 A a—4.32 A

material is transforming into the stable low-temperature phase. If, after heating to just below the transition temperature of 633°K, the MnBi is cooled, it then returns along the original curve of the low-temperature phase. It can be seen that upon extrapolation to $I_s=0$, a Curie point is found at about 470°K. Because of the inaccuracies involved, this second estimate of the Curie point of the high-temperature phase is considered to be in good agreement with the value derived from the reciprocal susceptibility curve. (The fact that the quenched form of MnBi is ferromagnetic was first observed in our Laboratories by Himmel and Jack.[6])

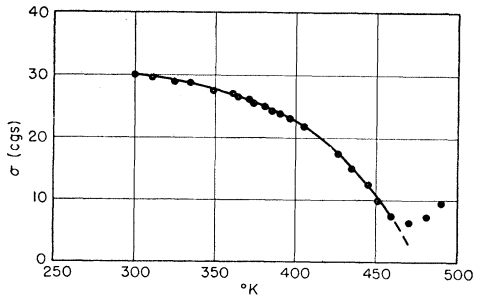

FIG. 3. Saturation magnetization of quenched MnBi.

ACKNOWLEDGMENTS

The author wishes to thank Miss Erlena Schilling for her work on the magnetic measurements.

[6] L. Himmel and K. Jack, (unpublished work).

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Heat Capacities of Vanadium and Tantalum in the Normal and Superconducting Phases*

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The heat capacities of two samples of vanadium and two of tantalum have been measured in the normal and superconducting phases in the temperature interval between 1.7° and 5°K. Below the transition temperature T_0, the superconducting heat capacity of both metals could be represented accurately by the relation $C_s=AT+BT^2$. In the normal phase the data obeyed the usual relation $C_n=\gamma T+(464/\theta^3)T^3$. From these data H *vs* T curves were calculated and values of H_0, the threshold field at absolute zero, were obtained. For the better vanadium sample the values of the various constants were found to be $T_0=4.89$°K, $A=-1.97\times10^{-3}$ cal/mole deg^2, $B=1.69\times10^{-3}$ cal/mole deg^3, $\gamma=21.1\times10^{-4}$ cal/mole deg^2, $\Theta=273$°K, and $H_0=1340$ oersteds; for the better tantalum sample $T_0=4.38$°K, $A=-1.45\times10^{-3}$ cal/mole deg^2, $B=1.33\times10^{-3}$ cal/mole deg^3, $\gamma=13.0\times10^{-4}$ cal/mole deg^2, $\Theta=231$°K, and $H_0=860$ gauss. The measured heat capacities were compared with the predictions of the Koppe theory and the α model.

1. INTRODUCTION

AN experimental study of the electronic contribution to the heat capacity of metals in the superconducting phase is of fundamental interest in the theory of superconductivity. Vanadium and tantalum are well suited to such a study for they have a high zero field transition temperature, a large electronic heat capacity, and a relatively small lattice heat capacity. In addition, the heat capacities of these two metals are of interest in their own right for comparison with the results of magnetic measurements of the threshold fields which destroy their superconductivity.

There is a great disparity in the threshold fields which have been reported for vanadium,[1,2] and, prior to the present measurements, no calorimetric data existed for the purpose of comparison. The more recent work[2] indicates that the threshold fields for this metal depend markedly on the amount of internal strain in the sample, due either to mechanical work or to the presence of interstitial gaseous impurities which distort the lattice structure. The effect of these quantities on the heat capacities of vanadium has been studied in these experiments.

Tantalum has been the subject of two earlier heat capacity investigations. The first of these was carried out by Keesom and Désirant in 1941.[3] Since their results did not agree with the magnetic measurements

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[1] Webber, Reynolds, and McGuire, Phys. Rev. **76**, 293 (1949).
[2] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952).
[3] W. H. Keesom and M. Désirant, Physica **8**, 273 (1941).

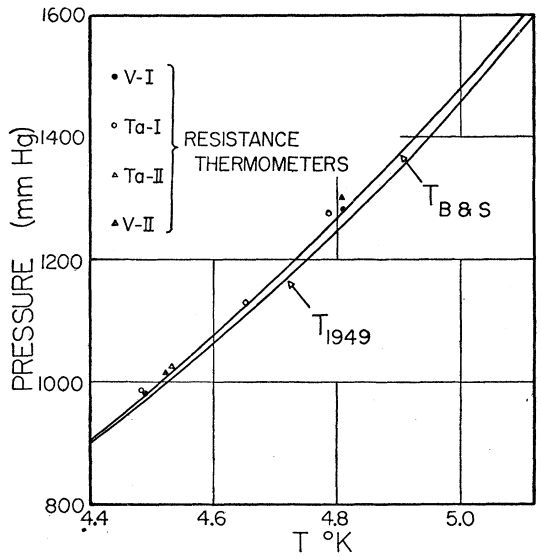

FIG. 1. The vapor pressure of helium between 4.4° and 5°K. T_{1949} is the relation given by the 1949 temperature scale; $T_{B\&S}$ is the relation determined by Berman and Swenson.

of Daunt and Mendelssohn,[4] particularly in the vicinity of the zero field transition temperature, Mendelssohn and Désirant[5,6] repeated the heat-capacity measurements in this temperature range on a sample of tantalum taken from the same batch as the sample used by Daunt and Mendelssohn. They obtained reasonable agreement with the magnetic measurements. Since the results of these two measurements of the heat capacity of tantalum are not in agreement and since the later measurements cover only a very limited temperature interval, it was deemed worth while to repeat the measurements in greater detail. No study of the effect of internal strain due to interstitial gaseous impurities or to mechanical work was attempted.

2. EXPERIMENTAL PROCEDURE

The experimental techniques and apparatus used in these measurements have been described in an earlier paper from this laboratory on the heat capacities of niobium.[7] The only modification of the apparatus described therein has been the addition of an improved system of manometers to increase the range and accuracy of the measurement of the vapor pressure of the liquid helium bath. This system consisted of a mercury manometer and a butyl phthalate oil manometer each 135 cm long and each equipped with brass scales and verniers. The oil manometer was used over the range of pressures from 0.1 to 9 cm Hg and the mercury manometer over the range from 9 to 135 cm Hg. Column heights were measured to 0.2 mm and corrected for the temperature variation of the density of the mercury and oil. To facilitate measurements at pressures above 76 cm Hg a heater at the bottom of the helium bath was used to warm the bath to the required temperature.

All vapor pressure measurements at temperatures above the λ point of liquid helium were corrected for the hydrostatic pressure of the liquid helium above the level of the resistance thermometer. Since the helium Dewar was not transparent, the height of the helium bath level was determined by measuring the efflux of helium gas with a flowmeter attached to the exhaust from the mechanical pumps. The initial bath level was established by completely filling the Dewar with liquid helium at the start of the experiment. Starting with a full Dewar the hydrostatic pressure correction was equivalent to 0.004° at the normal boiling point and to 0.040° after pumping the bath down to a temperature just above the λ point.

Each sample contained an Allen-Bradley carbon resistor whose resistance was measured at each vapor pressure determination. The conversion from vapor pressure to temperature and the calibration of these carbon resistance thermometers have been described in detail in a previous communication[8] which called attention to possible errors in the 1949 "agreed" relation[9] between vapor pressure and temperature above 4.2°K. These errors were later confirmed by Berman and Swenson[10] but found to be of smaller magnitude than those reported by us. When our data, however, were modified by the application of the Kistemaker[11] corrections the results were found to be in good agreement with those of Berman and Swenson, as shown in Fig. 1. The data obtained with four different resistance thermometers, each mounted in a different sample, are shown in Fig. 1 as separate points. The points obtained with each thermometer are designated according to the tabulation which will be given later in Table II.

The heat capacities were determined in the manner described by Brown, Zemansky, and Boorse[7] from the equation

$$C=(i_H)^2R_H\Delta\tau/nJ\Delta T, \tag{1}$$

where n is the number of moles, J the mechanical equivalent of heat, i_H the heater current, R_H the heater resistance, $\Delta\tau$ the time interval during which energy was supplied to the heater, and ΔT the temperature difference brought about by this energy input. ΔT was obtained from the relation

$$\Delta T=\frac{\Delta R}{dR/dT} \tag{2}$$

[4] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).
[5] K. Mendelssohn, Nature **148**, 316 (1941).
[6] M. Désirant, *Report of the International Conference on Fundamental Particles and Low Temperatures* (Physical Society, London, 1947), Vol. 2, p. 124.
[7] Brown, Zemansky, and Boorse, Phys. Rev. **92**, 52 (1953).
[8] Worley, Zemansky, and Boorse, Phys. Rev. **93**, 45 (1954).
[9] H. van Dijk and D. Shoenberg, Nature **164**, 151 (1949).
[10] R. Berman and C. A. Swenson, Phys. Rev. **95**, 311 (1954).
[11] J. Kistemaker, Physica **12**, 272 (1946).

where ΔR is the change in the resistance of the thermometer during the heating interval and dR/dT is the slope of the calibration equation described earlier.[8] In all of the measurements i_H was chosen to make the energy input at least ten times the natural heat leak, and ΔR was then chosen to make $\Delta\tau$ of the order of 10 to 30 seconds.

i_H, R_H, and $\Delta\tau$ were each measured to better than 0.1 percent. Errors in these three quantities were unimportant compared to those introduced into the measurements through dR/dT and ΔR. Errors in dR/dT were due primarily to systematic errors in calibrating the resistance thermometers. At worst, an error of 0.02° at 5°K would introduce an error of 1.5 percent in the heat capacity at that temperature. Such systematic errors should not appreciably affect the comparison of the results obtained for different samples since all thermometers were calibrated in the same manner and the errors in calibration should be much the same for all. The uncertainty in reading ΔR from the heating curves was of the order of 1 percent. The corresponding uncertainty in the curve of heat capacity as a function of temperature, obtained from a large number of heat capacity determinations, should be much smaller if the errors in ΔR were random. They were not completely random since personal judgment was required for the extrapolation of the fore and after periods of the heating curves. Consequently the use of the method of least squares, which will be described in the presentation of the results, must be regarded merely as a systematic method for handling the data. For this reason no attempt was made to compute precision measures for the least square calculations. From these considerations it is estimated that for the purpose of intercomparison the results are good to better than 1 percent, while the absolute values for the heat capacities are good to better than 2 percent. For the smaller sample of tantalum these figures should be increased to 2 percent and 3 percent, respectively, for in these measurements the slopes of the fore and after periods of the heating curves were steeper and ΔR could not be read with as great accuracy.

The contributions to the heat capacity of each sample from the resistance thermometer and from the glyptal varnish used to bond the thermometer and heater to the sample were estimated from the data of Gurney[12] for the heat capacity of carbon and from that of Keesom and Pearlman[13] for the heat capacity of glyptal. These contributions were of the order of 2 percent for the small tantalum sample and appropriate corrections were made. No corrections were made to the measured heat capacities of the other samples since the contributions were at most 0.6 percent and were very nearly equal for all samples.

TABLE I. Properties of vanadium and tantalum samples.

Sample	No. of moles	Density (g/cm³)	% impurities (by weight) N_2	O_2	H_2	C	Fe
V–I	3.802	6.098	0.132	0.13	0.0055	0.045	0.1
V–II	2.674	6.098	0.04	0.08	0.008	0.054	···
V–IIA	2.650	6.100	0.04	0.08	0.0005	···	···[a]
			0.05	0.05	0.001	···	···[b]
Ta–I	3.029	16.09	···	···	···	0.03	0.03
Ta–II	0.5545	16.65	···	···	···	0.03	0.03

[a] Center of bar.
[b] Surface layer.

TABLE II. Characteristics of resistance thermometers.

Sample	Nominal resistance (ohms)	Power dissipation (watts)	Room temperature resistance (mounted in sample) (ohms)	Approx. resistance at NBP of helium (ohms)
V–I	22	1	36	335
V–II	27	½	37	465[a]
V–IIA	27	½	37	465[a]
Ta–I	27	1	43	605
Ta–II	27	½	35	435

[a] The same thermometer was used for both series of measurements.

3. EXPERIMENTAL RESULTS

A. Description of Samples

The physical properties of the samples of vanadium and tantalum used in these experiments are given in Table I. Table II gives the characteristics of the resistance thermometers used in the various samples.

The vanadium samples were supplied by the Union Carbide and Carbon Corporation. Each was forged under atmospheric conditions to a one-inch diameter bar from a two-inch square ingot at a temperature of 1125°C. The finishing temperature for this process was 750°C. After cooling in air the surface oxide layer was machined away. Since the recrystallization temperature for vanadium is about 750°–800°C, the samples presumably contain a considerable amount of stress due to cold-working. The analysis of nonmetallic impurities was made by the Union Carbide and Carbon Research Laboratories. A spectrographic analysis of turnings from sample V–I was made by the Analytical and Research Measurements Laboratories of the Department of Chemistry of Columbia University. This analysis indicated that, with the exception of iron, metallic impurities were present in amounts of 0.01 percent or less.

Preliminary heat capacity measurements were made on sample V–I in the condition in which it was received. The measurements were repeated after annealing the sample at a temperature of 950°C for 10 hours at a pressure below 10^{-5} mm Hg. In the interim between the measurements the accuracy of the measurement of temperature was greatly improved by the installation of the new manometer system. Within the accuracy of the earlier measurements no significant changes were

[12] R. W. Gurney, Phys. Rev. 88, 465 (1952).
[13] P. H. Keesom and N. Pearlman, Phys. Rev. 88, 398 (1952).

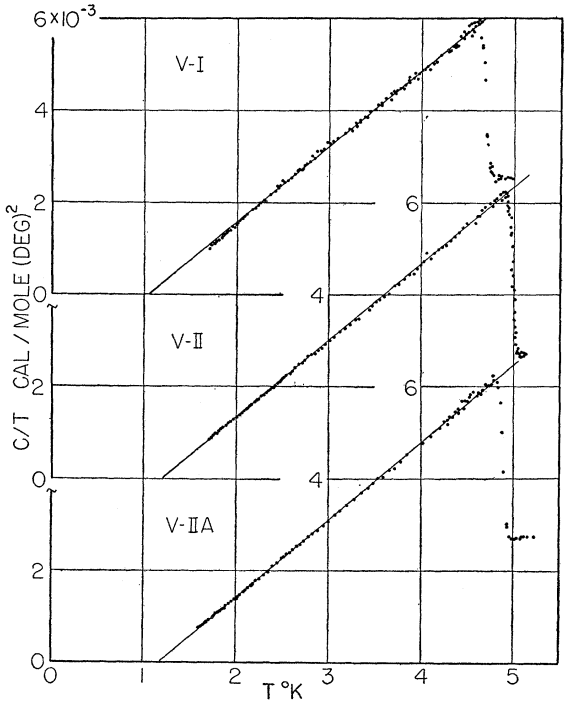

FIG. 2. *C/T versus T* for the vanadium samples in the superconducting phase.

observed in the heat capacity of the vanadium sample. In particular, the zero field transition temperature, which later measurements showed to be quite sensitive to changes in physical properties, was not affected.

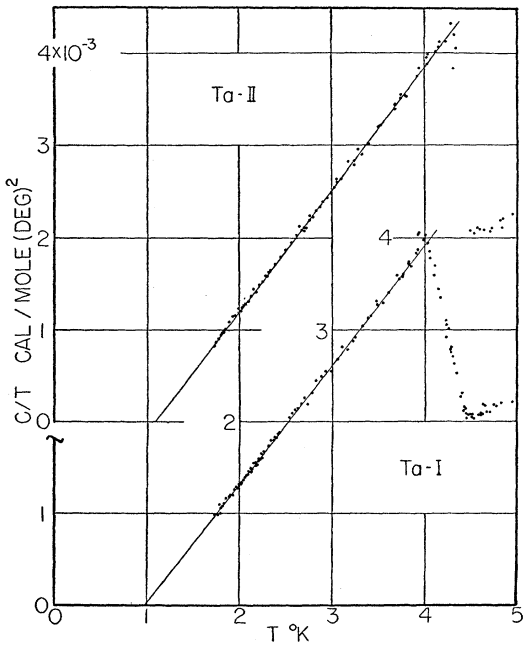

FIG. 3. *C/T versus T* for the tantalum samples in the superconducting phase.

The results which are reported for this sample are those obtained after the heat treatment.

A similar series of measurements were carried out on a vanadium sample of higher purity. This sample is designated in the table as V–II before annealing and as V–IIA after annealing. In view of the results of the measurements on sample V–I it was decided that this second sample should be annealed at a temperature just below the melting temperature, 1900°C.[14] Since this temperature was well beyond the range of the available furnace, arrangements were made with the Materials Laboratory of the Wright Air Development Center at Wright-Patterson Air Force Base, Ohio, to carry out the heat treatment in their resistance furnace. In the annealing cycle the sample was heated to a temperature of 1800°C in thirty minutes, held at that temperature for one hour, and then cooled without quenching in twenty minutes. The pressure throughout the cycle was 4×10^{-4} mm Hg. After this heat treatment the sample consisted of polycrystals with a grain size of 1 to 2 mm easily visible to the unaided eye. Originally gray, the sample had acquired a yellowish luster. The Materials Laboratory ascribed the change in color to a slight pickup of oxygen or nitrogen at the end of the heating cycle when the furnace was opened to the atmosphere. At the conclusion of the second series of heat capacity measurements the sample was returned to the Union Carbide and Carbon Research Laboratories for an analysis of gas content. Samples for the analysis were taken from a surface layer, after hand polishing to remove the temper color, and from the center of the bar. The results of the analysis are included in Table I. They indicate a definite reduction in the hydrogen content. The oxygen content was reduced in the surface layer, although this figure can probably be taken as an indication of no change. There was no change in the nitrogen content.

The tantalum samples were purchased from the Fansteel Metallurgical Corporation, the only commercial source of tantalum. Massive tantalum metal is prepared commercially by compacting electrolytic powder at moderate pressures and then sintering in vacuum. The bar is purposely left rather porous to enable the hydrogen which is evolved during sintering to escape. Hydrogen is not present in the original electrolytic powder but is absorbed by the metal during the chemical cleaning process preparatory to compacting and sintering. After sintering, the metal is worked to higher density by cold swaging and rolling until there is a considerable reduction in cross section. The larger rod sizes cannot be supplied at the proper density because Fansteel is not able to effect the necessary reduction. When the bar has been worked to the proper size it is annealed at 1150°C at a pressure of 5×10^{-6} mm Hg. In order to minimize cold-working,

[14] Adenstadt, Pequiquot, and Raymer, Trans. Am. Soc. Metals 44, 990 (1952).

considerable care was exercised in the machining necessary to prepare the samples for the heat capacity measurements. The initial measurements were made on the larger sample of low density. Because this sample did not exhibit a sharp transition from the superconducting to the normal phase in the absence of a magnetic field, further measurements were made on the smaller sample with the proper density. The impurities quoted in Table I do not refer to these particular samples but are merely typical of tantalum metal refined by Fansteel. No estimate of gaseous impurities was available.

B. Results of the Heat-Capacity Measurements

The experimental results for the heat capacities in the superconducting phase for all the samples are shown in Figs. 2 and 3. The data are presented as plots of C_s/T *versus* T, where C_s is the superconducting heat capacity in calories per mole-degree. This form of presentation was chosen because it was found that the

TABLE III. Coefficients for Eq. (3) and zero field transition temperatures.

Sample	A (cal/mole deg²)	B (cal/mole deg⁴)	T_0 (°K)	Width of transition (°K)	Number of points
V–I	-1.73×10^{-3}	1.65×10^{-3}	4.69	4.66–4.85	129
V–II	-2.01×10^{-3}	1.67×10^{-3}	4.99	4.93–5.05	115
V–IIA	-1.97×10^{-3}	1.69×10^{-3}	4.89	4.82–4.96	99
Ta–I	-1.26×10^{-3}	1.29×10^{-3}	···	4.02–4.42	83
Ta–II	-1.45×10^{-3}	1.33×10^{-3}	4.38	4.36–4.41	77

equation

$$C_s=AT+BT^2 \tag{3}$$

describes the experimental results remarkably well in the temperature range covered by the measurements. The coefficients of Eq. (3) were obtained from the data by a least-squares fit to a straight line on the plot of C_s/T *versus* T, assuming that errors were present only in the y-coordinate. These coefficients are given in Table III, and the lines which they represent are shown in the figures. The number of experimental points used in each least squares calculation is also tabulated. It is emphasized that Eq. (3) cannot be valid at much lower temperatures since the parameters given in the table yield a negative heat capacity below 1°K. Table III also contains a tabulation of the zero-field transition temperature, T_0, for each sample and the approximate width of the transition region. In this tabulation, T_0 is defined as that temperature at which the heat capacity is midway between the values in the normal and superconducting phases.

The normal data for each sample are shown in Figs. 4 and 5, where C_n/T is plotted against T^2. C_n is the heat capacity in the normal phase in calories per mole-degree. These data were obtained in applied fields of 5000 gauss, although some of the results for

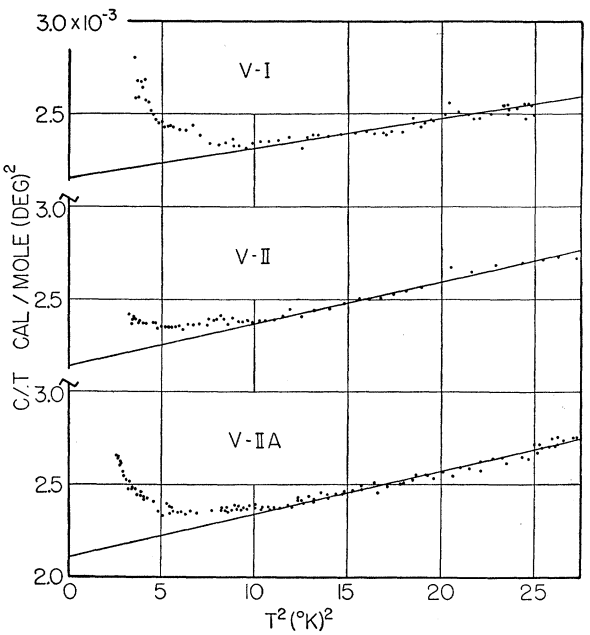

FIG. 4. C/T *versus* T^2 for the vanadium samples in fields of 5000 gauss.

Ta–II at the lower temperatures were obtained in smaller fields. The straight line on each plot represents the equation

$$C_n=\gamma T+(464/\Theta^3)T^3. \tag{4}$$

This is the Debye-Sommerfeld relation which expresses the heat capacity as the sum of a term linear in T representing the electronic contribution and a term cubic in T representing the lattice contribution. Θ is the Debye characteristic temperature. γ and Θ were obtained from the data by a least-squares fit to a straight

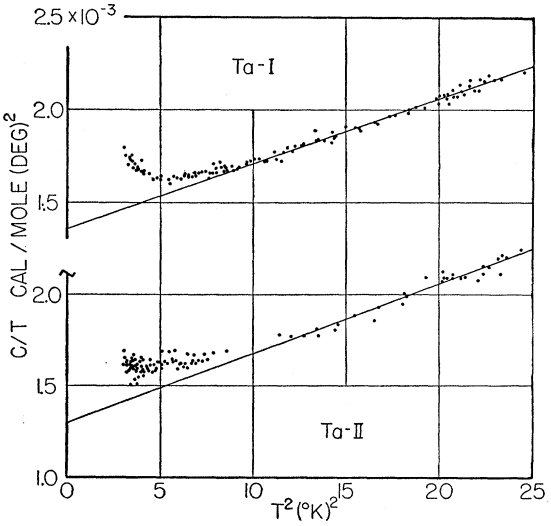

FIG. 5. C/T *versus* T^2 for the tantalum samples in fields of 5000 gauss. Below $T^2=10$ some of the data for sample Ta–II were obtained in smaller fields.

line on the plot of C_n/T *versus* T^2, again assuming that errors were present only in the y-coordinate. The range in T^2 over which the data was fitted to a straight line was limited to that region in which the data was reasonably linear. The values of γ and Θ for each sample are given in Table IV. The interval in T^2 used in fitting Eq. (5) to the data and the number of points used in the least-squares calculations are also tabulated. For sample V–I and for the tantalum samples these values of γ and Θ supercede those which were reported earlier.[15,16] The earlier values for tantalum were based on the 1949 temperature scale without the Kistemaker corrections.

At the lower temperatures, the normal heat capacities of all the samples exceeded the values given by Eq. (4). This behavior suggests that the applied magnetic field was not large enough to destroy completely superconductivity and that each sample was undergoing the transition from the superconducting to the normal phase as its temperature increased during the sequence of heat capacity determinations. When the transition from super to normal conductivity takes place in a magnetic field a latent heat is absorbed. If the superconductor has a zero demagnetizing coefficient and if the magnetic field is uniform, then the transition will take place in an infinitesimal temperature interval and the apparent heat capacity will be infinitely large. If the field is not homogeneous or if the demagnetizing coefficient is not zero the transition will be spread over a finite temperature interval. In this temperature interval the sample is in a mixed phase, partially normal and partially superconducting, called the intermediate state. As the sample passes through the intermediate state its heat capacity will rise above that in the superconducting phase, pass through a maximum, and descend to the value appropriate to the normal phase. If the magnetic field is increased and the process repeated, the position of the maximum will be shifted to lower temperatures. Because the samples used in these experiments had a demagnetizing coefficient greater than $\frac{1}{2}$, and because the applied magnetic field was not homogeneous over the region occupied by the sample, the intermediate state would be spread over a wide range in temperature if the magnetic field were not sufficient to destroy completely superconductivity.

To determine if the intermediate state were present in these samples at the largest field strengths employed, a series of measurements of the heat capacities of three of the samples were made at lower field strengths. The results for samples V–IIA and Ta–I are shown in Figs. 6 and 7 as plots of C/T *versus* T^2. The preceding discussion of the behavior of C as a function of T applies equally well to C/T as a function of T^2. In Fig. 7, it may be seen that the curve for Ta–I in a field of 500 gauss behaves in the manner just described. Although the complete curve for the heat capacity in the intermediate state was not traced out for each of the magnetic fields that was used, it is possible to estimate the position of the maximum in the curve from the measurement of a small portion of the curve. The results for V–IIA show that the maximum was shifted to lower temperatures as the applied field was increased, for all values of the field. This confirms that the intermediate state was present in the vanadium sample at the lower temperatures for all field strengths and that at the lowest temperature superconductivity was never completely destroyed. A similar behavior has been observed by Goldman[17] who has made magnetic measurements at low temperatures and high field strengths on the samples of vanadium used by Wexler and Corak.[2] He found evidences of superconductivity in fields as large as 6000 gauss at 2°K. These results

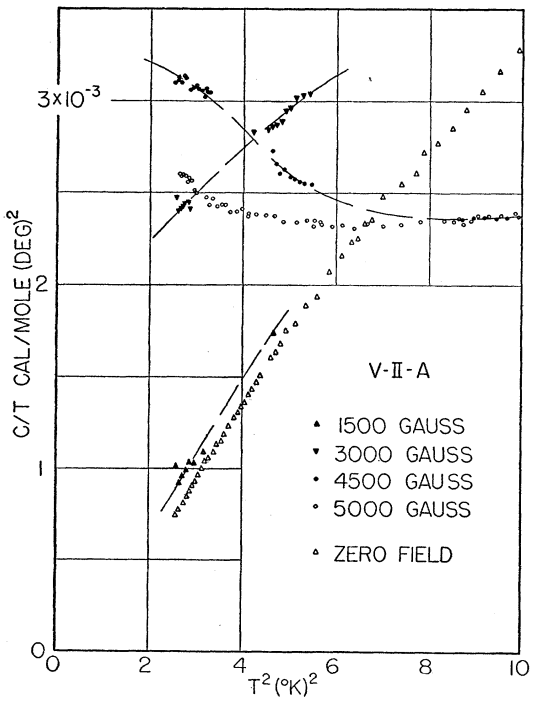

FIG. 6. C/T *versus* T^2 for sample V–IIA in the intermediate state.

TABLE IV. Electronic constants and Debye temperatures.

Sample	γ (cal/mole deg²)	Θ (°K)	Range in T^2 (°K²)	Number of points
V–I	21.5×10^{-4}	308	12.5–25	32
V–II	21.4×10^{-4}	274	12.5–25	18
V–IIA	21.1×10^{-4}	273	12.5–25	49
Ta–I	13.6×10^{-4}	237	9 –25	65
Ta–II	13.0×10^{-4}	231	11 –25	32

[15] J. Eisenstein, Revs. Modern Phys. **26**, 277 (1954).
[16] Worley, Zemansky, and Boorse, Phys. Rev. **93**, 1567 (1953).
[17] J. E. Goldman, remarks at Third International Conference on Low Temperature Physics and Chemistry (Rice Institute, Houston, 1953).

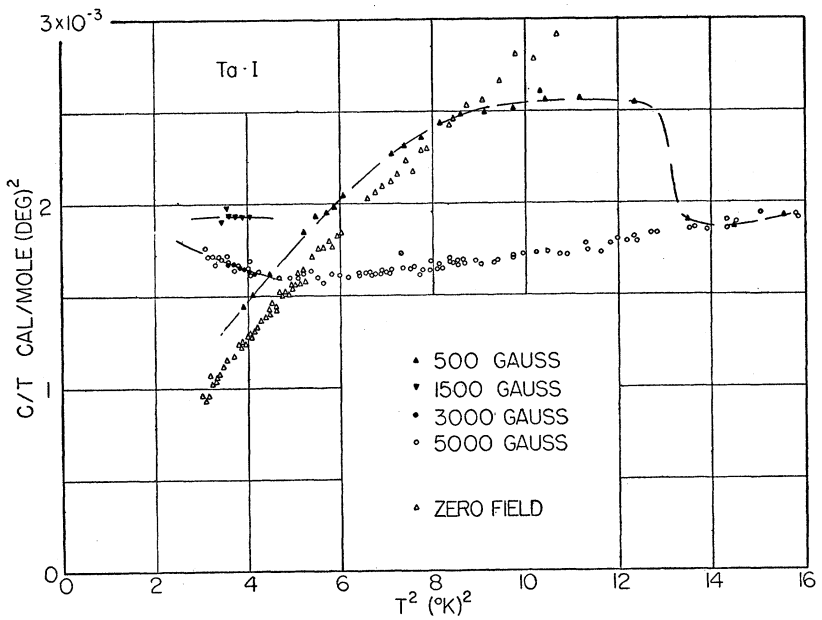

FIG. 7. C/T *versus* T^2 for sample Ta–I in the intermediate state.

show that a magnetic field larger than the one currently available is necessary if the heat capacity measurements in the normal phase on the vanadium samples used in these experiments are to be extended below 3°K.

The results of the measurements on the two tantalum samples are not as readily interpreted in terms of the intermediate state. For sample Ta–I in fields lower than 3000 gauss the maximum in the heat capacity was indeed shifted to lower temperatures as the field was increased. In larger fields, however, the maximum was no longer shifted and the heat capacity was independent of the magnetic field. For Ta–II no systematic variation with field strength was observed in the heat capacity in fields of 1200, 2800, and 5000 gauss within the precision of the measurements. The results of all the measurements made on this sample at different field strengths have been plotted in Fig. 5. Although the results for both samples show no variation with field strength for sufficiently large fields, nevertheless the heat capacities at the lowest temperatures are larger by about 20 percent than the values given by Eq. (4) using the constants from Table IV.

4. DISCUSSION

A. Calculation of the H_T *versus* T Curve

The heat capacities in the normal and superconducting phases are related to the threshold field H_T by the equation

$$C_s-C_n=\frac{VT}{4\pi}\frac{d}{dT}\left(H_T\frac{dH_T}{dT}\right); \quad (5)$$

V is the molar volume. If Eqs. (3) and (4) are used for C_s and C_n, then H_T can be obtained as a function of temperature in a straight forward manner by dividing Eq. (5) by T and integrating twice with respect to the temperature from T_1 to T_0, where T_1 is the lowest temperature attained in the calorimetric measurements. The constants of integration are evaluated by putting $T=T_0$ after each integration. The threshold fields which are obtained for samples V–II and Ta–II are given by

$$\text{V–II: } H_T=10\{17\,680+1077T-2621T^2+351.5T^3-2.38T^4\}^{\frac{1}{2}}, \quad 1.7°<T<4.99°\text{K}; \quad (6)$$

$$\text{Ta–II: } H_T=10\{6997+366.8T-1327T^2+214.0T^3-3.05T^4\}^{\frac{1}{2}}, \quad 1.7°<T<4.38°\text{K}. \quad (7)$$

V–II was chosen for this calculation because its transition temperature, purity, and mechanical state most nearly resembled those of the vanadium sample for which an H_T *versus* T curve was obtained by Wexler and Corak[2]; Ta–II was chosen because it exhibited a much sharper zero field transition than Ta–I. The results for both metals are plotted as H_T *versus* T^2 in Fig. 8. This type of plot was used since it shows most clearly the departures from the parabolic relation $H_T=H_0(1-T^2/T_0^2)$ which is often used to represent the threshold fields of superconductors. The points representing the magnetic measurements on vanadium are the results of Wexler and Corak for their sample B. Those for tantalum are the smoothed values of Daunt and Mendelssohn[4] corrected to the 1949 temperature scale by Shoenberg.[18]

The value of the threshold field at absolute zero, H_0, and the slope of the threshold field curve at T_0 are

[18] D. Shoenberg, *Superconductivity* (Cambridge University Press, London 1952), pp. 224–227.

also of interest since these quantities, together with T_0, are customarily used to report the results of magnetic measurements on superconductors. They are easily obtained from Eq. (5). To solve for H_0 the equation is integrated with respect to the temperature from 0°K to T_0, integrating the right-hand member by parts:

$$\int_0^{T_0}(C_s-C_n)dT=\frac{V}{4\pi}\left\{TH_T\frac{dH_T}{dT}\Big|_0^{T_0}-\tfrac{1}{2}\int_0^{T_0}\frac{dH^2_T}{dT}dT\right\}.$$

The first term on the right-hand side vanishes at both limits, so that

$$\int_0^{T_0}(C_s-C_n)dT=\frac{VH_0^2}{8\pi}. \tag{8}$$

To apply this equation to the experimental data C_s and C_n must be extrapolated to absolute zero. The exact nature of the extrapolation of C_s is not critical since the area under this portion of the curve is only a small fraction of the total area. Equation (4) is assumed to be correct for C_n over the entire temperature interval. $(dH_T/dT)_{T=T_0}$ follows directly from Eq. (5) when the indicated differentiation is performed. Since H_T is zero when $T=T_0$, Eq. (5) reduces to Rutgers' equation,

$$(C_s-C_n)_{T=T_0}=\frac{VT_0}{4\pi}\left\{\frac{dH_T}{dT}\right\}^2_{T=T_0}. \tag{9}$$

The results for the three vanadium samples and the small sample of tantalum are assembled in Table V. Included for comparison are the values for sample B of Wexler and Corak and the values for tantalum of Daunt and Mendelssohn as corrected by Shoenberg. A complete summary of the work on tantalum prior to 1947 has been given by Webber.[19] Much of this has been done by measuring the resistance of the sample to detect the onset of superconductivity. While resistance measurements can be of value when comparing the effects of purity and annealing on the behavior of tantalum, the magnetic measurements of Daunt and Mendelssohn are presumed to represent more closely the equilibrium values of the threshold fields. Work on vanadium has not been as extensive. Since its superconductivity was discovered by Meissner and Westerhoff in 1935,[20] the only other work has been that of Webber, Reynolds, and McGuire.[1] They found very broad transitions and very large critical fields, of the order of 10 000 gauss at 2°K, for two samples. Their measurements of the threshold field curve were not as detailed as those of Wexler and Corak.

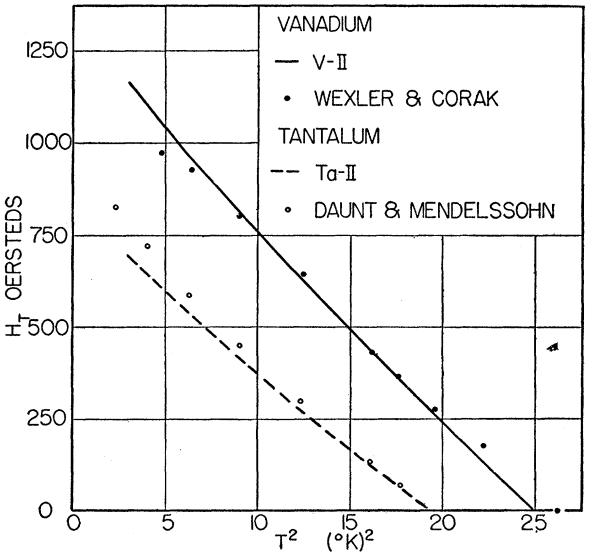

FIG. 8. Threshold fields for vanadium and tantalum. The curves represent the fields calculated from the calorimetric data; the individual points represent the results of magnetic measurements.

TABLE V. Magnetic properties of superconducting vanadium and tantalum.

Sample	T_0 (°K)	H_0 (gauss)	$(dH/dT)_{T=T_0}$ (gauss/deg)
Vanadium			
V-I	4.69	1260	−471
V-II	4.99	1360	−477
V-IIA	4.89	1340	−482
Wexler and Corak[a]	5.13	1190	−436
Tantalum			
Ta-II	4.38	860	−334
Daunt and Mendelssohn[b,c]	4.4	975	−310

[a] Reference 2.
[b] Reference 4.
[c] Values corrected to 1949 temperature scale by Shoenberg, reference 18.

B. Effects of Purity and Annealing on the Heat Capacity of Vanadium

Vanadium is typical of the so-called hard superconductors whose properties depend strongly on the chemical and physical state of the metal. As a rule the hard metals have very high melting points so that it is difficult to prepare samples of high purity, and once prepared it is difficult to anneal them without contamination. Presumably the distinction between hard and soft superconductors would vanish if each could be obtained in an ideal state, i.e., a single crystal. The present investigation of the effects of purity and mechanical state on the heat capacity of vanadium was launched in an effort to ascertain if the differences in properties from sample to sample observed in magnetic measurements would be reflected in the heat capacity, and if they were, to obtain data for a sample which most nearly approximated the ideal case for the purpose of comparison with theory.

[19] R. T. Webber, Phys. Rev. **72**, 1241 (1947).
[20] W. Meissner and H. Westerhoff, Z. Physik **87**, 206 (1934).

The results of the measurements show that C_n, C_s, and T_0 are all sensitive to the state of the sample. The closest correlation between these results and those of magnetic measurements arises in the behavior of T_0 as a function of purity. Wexler and Corak observed that the zero field transition temperature of vanadium was markedly dependent on the amount of nitrogen and oxygen present in the sample; in small concentrations these strain the lattice by entering the structure interstitially. The correlation between transition temperature and purity is shown in Table VI. Since the measurements do not distinguish between the effects of nitrogen and oxygen impurities, the sum of these impurities has been tabulated in the last column as an aid in making the correlation. Wexler and Corak did not report a threshold field curve for all of their samples, so that in the preparation of this table the transition temperature for samples *D* and *E* were obtained directly from their *B versus H* curves; the spread in temperature given in the table represents the interval which bracketed T_0 in the actual measurements and does not relate to the actual width of the transition. These authors reported the same transition temperature for their samples *A*, *B*, and *C*. Since the purities of these samples did not differ appreciably, only sample *B* is included in the table. The transition temperature of sample *D* probably lies near the lower limit given in the table. Since the sample was melted in its preparation it is not surprising that its transition temperature lies below that of sample V–I in view of the effect of annealing on the transition temperature of vanadium which was observed in the present measurements.

The depression of the zero field transition temperature of sample V–II following the removal of mechanical strains by annealing was unexpected. Many independent investigators have found just the opposite effect for the hard superconductors niobium[21] and tantalum.[19,22,23] Since all three metals are found in the same column in the periodic table and all have very similar superconducting and physical properties, one might expect their transition temperatures to respond in a similar way to the amount of cold work present. It must be noted, however, that with the exception of niobium and tantalum, the reduction of T_0 with the removal of cold work is typical of most superconductors; it has been observed for zirconium[24] and thorium[25] among the hard superconductors, and for tin,[26] thallium,[26] indium,[26,27] and mercury[27] among the soft.

Changes in the amount of impurity and the amount of cold work present in the vanadium samples produced small but measurable changes in the superconducting heat capacity, while only changes in the amount of impurity affected the normal heat capacity. In the normal phase, within the accuracy of the measurements, there was no change in the electronic heat capacity. The small differences in γ among the three samples are not deemed significant in view of the rather long extrapolation necessitated by the presence of the intermediate state at lower temperatures. The change in the Debye Θ with purity is in the direction to be expected from simple Debye theory. Although no measurements of the elastic constants of vanadium are available, it is known that the hardness of the metal increases with increasing oxygen and nitrogen content.[28] Since the Debye Θ is proportional to the velocity of sound, it will be larger for the sample in which the velocity is greater, that is the harder, and more impure sample. The behavior of the Debye Θ indicates that the impurities in vanadium are the primary cause of internal strains. Thus it is not surprising that the intermediate state persisted in very high fields in the annealed vanadium sample, since this behavior is typical of severly strained superconductors.[29] The insensitivity of Θ to the large change in hydrogen impurity which resulted from the high vacuum anneal is an indication that small amounts of hydrogen do not appreciably distort the lattice structure.

TABLE VI. The effect of oxygen and nitrogen impurities on the zero field transition temperature of vanadium.

Sample	T_0 (°K)	% impurities (by weight) O_2	N_2	O_2+N_2
Wexler and Corak[a] Sample *B*	5.13	0.038	0.021	0.059
V–II	4.99	0.08	0.04	0.12
V–IIA	4.89	0.08	0.04	0.12
Wexler and Corak[a] Sample *D*	4.60–4.70	0.075	0.106	0.181
V–I	4.69	0.13	0.132	0.262
Wexler and Corak[a] Sample *E*	4.11–4.19	0.15	0.189	0.339

[a] Reference 2.

C. Intermediate State Measurements on Tantalum

The calculations described earlier yielded values for the threshold fields several times smaller than those actually applied to the samples during the heat capacity measurements. Yet the results for samples V–IIA and Ta–I show that the application of fields larger than the threshold values will not guarantee the destruction of superconductivity. For sample Ta–I, a more realistic estimate of the fields necessary to destroy superconductivity completely can be made by utilizing the results of the measurements in a field of 500 gauss.

[21] L. C. Jackson, *Proceedings of the International Conference on Low Temperature Physics* (Oxford, 1951), p. 16.
[22] Silsbee, Scott, and Brickwedde, J. Research Natl. Bur. Standards **18**, 295 (1937).
[23] Ziegler, Brucksch, and Hickman, Phys. Rev. **62**, 354 (1942).
[24] T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952).
[25] D. Shoenberg, Proc. Cambridge Phil. Soc. **36**, 84 (1940).
[26] W. I. Khotkevitch and V. R. Golik, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 427 (1950).
[27] E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).
[28] S. Beatty, J. Metals **4**, Trans., 987 (1952).
[29] B. G. Lasarew and A. A. Galkin, J. Phys. (U.S.S.R.) **8**, 371 (1944).

TABLE VII. Calorimetric properties of normal and super-conducting tantalum.

Sample	γ $\left(\frac{\text{cal}}{\text{mole deg}^2}\right)$	Θ (°K)	A $\left(\frac{\text{cal}}{\text{mole deg}^2}\right)$	B $\left(\frac{\text{cal}}{\text{mole deg}^3}\right)$	T_0 (°K)	Purity (%)
Ta–I	13.6×10^{-4}	237	-1.26×10^{-3}	1.29×10^{-3}	4.02–4.42	99.9+
Ta–II	13.0×10^{-4}	231	-1.45×10^{-3}	1.33×10^{-3}	4.36–4.41	99.9+
Keesom and Désirant[a]	14.1×10^{-4}	246	-1.14×10^{-3}	1.22×10^{-3}	3.96–4.16	99.95
Mendelssohn[b] and Désirant[c]	...	...	...	...	4.36–4.40	99.9+
Chou and White[d]	13.6×10^{-4}	250	-1.45×10^{-3}	1.33×10^{-3}	4.39[e]	...

[a] Reference 3.
[b] Reference 5.
[c] Reference 6.
[d] Reference 30.
[e] The width of the transition was not reported.

The disappearance of superconductivity in this field at 3.6°K determined a point on the H–T curve. Using the relation $H=H_0(1-T^2/T_0^2)$ and taking T_0 equal to 4°K, one obtains a value of 2700 gauss for H_0. Although no other H–T points were obtained in this manner, these parameters are consistent with the observations that superconductivity persisted in a field of 1400 gauss at 2°K while it was destroyed in a field of 2600 gauss at 1.7°K. This H–T curve is strong evidence against the presence of the intermediate state in the tantalum samples in fields of 5000 gauss. If the behavior of C_n was not due to the presence of the intermediate state, sample Ta–II comes closer to being an ideal sample, for 1200 gauss was sufficient to destroy superconductivity at 1.7°K and even smaller fields may have been adequate.

D. Comparison with Other Heat Capacity Measurements

In view of the anomalous behavior of C_n for both tantalum samples it is particularly instructive to compare these results with those of other measurements of the heat capacity of tantalum. Since the inception of the present experiments the results of Chou and White[30] for a sample of tantalum annealed in high vacuum at 2400°C have become available in addition to those of the references cited in the introduction. The results for all samples are assembled in Table VII. γ and Θ for C_n are those quoted by the original authors. A and B for C_s were obtained from the results of Keesom and Désirant[3] and of Chou and White by replotting their data as C_s/T *versus* T and drawing a straight line through the points. The agreement for Ta–II and the sample of Chou and White is striking, although the fit of their data to the straight line at temperatures near T_0 is not as good as at lower temperatures. The purity of each sample has been tabulated, but in the absence of an analysis of gaseous impurities it is not particularly significant. No information was given on the mechanical state of the samples of Keesom and Désirant and of Mendelssohn and Désirant; presumably they were unannealed.

At very low temperatures and in large magnetic fields, a rise in C_n/T was not observed for any of the other samples. Keesom and Désirant carried out their measurements in a field of 3000 gauss. The scatter of their data did not preclude such a behavior, but if present, it was of smaller magnitude than that observed for Ta–I and for Ta–II. The critical fields necessary to destroy superconductivity in their sample were very similar to those for Ta–I; measurements of the heat capacity in fields of 450 and 700 gauss showed that superconductivity was destroyed at 3.79° and 3.55°K respectively. Chou and White measured C_n in a field of 2000 gauss. They did not find a rise in C_n/T but they made only 6 determinations of the heat capacity below 3°K. They also observed the disappearance of superconductivity in smaller magnetic fields and found good agreement with those calculated from the calorimetric measurements.

In discussing the behavior of C_n for these samples it is instructive to review the results obtained by Webber for the effects of annealing and gaseous impurities on the superconducting properties of tantalum.[19] Making resistance measurements on tantalum wires near T_0, Webber observed that an anneal by the supplier, the Fansteel Metallurgical Corporation, at 1000°C was ineffectual. He was able, however, to raise the transition temperature from 4.16° to 4.30°K by additional annealing at 2400°C and to reduce $dH/dT)_{T=T_0}$ from -1200 to -600 gauss per degree. Measurements on another sample, which was annealed at 2400°C and then contaminated by heating to 1200°C and exposing to air at 10^{-3} mm Hg, yielded values of 4.32°K and -600 gauss per degree for T_0 and $dH/dT)_{T=T_0}$. The sample had absorbed an estimated 9 volumes of oxygen. Webber concluded that the state of anneal was the predominant factor influencing the superconducting properties of tantalum. Bearing in mind that Chou and White found agreement between

[30] C. Chou and D. White, Eighth Annual Calorimetry Conference, Chicago, Sept. 1953 (unpublished). The authors are indebted to Dr. Chou and Dr. White for making their results available prior to publication.

the threshold fields calculated from their calorimetric data and those which destroyed the superconductivity of their sample, one would surmise that their sample was the best of those which have been studied and that the rise in C_n/T at low temperatures is not typical of an ideal sample of tantalum. Indeed, Eq. (4) has proven adequate to describe the heat capacities of most metals, including superconducting metals in the normal phase, which have been studied in the helium temperature region. For this reason the departure of C_n from Eq. (4) has been neglected in the calculations of the threshold fields for Ta–II. If it were not neglected the derived H–T curve would be slightly depressed at lower temperatures.

Corak, Goodman, Satterthwaite, and Wexler[31] have recently reported the results of heat capacity measurements on a sample of vanadium in the superconducting phase over the temperature range from 1.2°K to its transition temperature at 5.05°K. They compared their results with those of the present measurements and found good agreement in the temperature interval common to both measurements. A more detailed comparison will not be attempted here. They fitted their data to an exponential dependence on temperature which represents their results to 5 percent or better from 1.2° to 4.5°K. Above this temperature range the fit is not as good.

E. The Two-Fluid Model of Superconductivity

These experimental results will be compared with two theoretical calculations, each of which has been carried out within the framework of the two-fluid model of superconductivity. This model was proposed by Gorter and Casimir[32] in 1934 to describe the second order phase transition in zero field and the temperature dependence of the threshold field and the heat capacity. The superconducting phase is envisaged as a mixture of two electronic fluids, the superconducting fluid which carries no entropy and the normal fluid which carries the entropy

$$S_n = K(\omega)\gamma T. \tag{10}$$

As the temperature is lowered below T_0 the electrons are presumed to condense from the normal into the superconducting fluid. ω is the degree of condensation; it varies from 1 at 0°K to 0 at T_0. $K(\omega)$ measures the effect of the condensation on the normal fluid; it is proportional to the effective number of normal electrons and varies from 0 at 0°K to 1 at T_0. At and above T_0, S_n is just γT, the electronic entropy given by the free electron theory of metals. Gorter and Casimir assumed that $K(\omega)=(1-\omega)^\alpha$, and, by assigning to α the constant value $\frac{1}{2}$, they obtained the parabolic threshold field curve and the heat capacity in the superconducting phase proportional to T^3, in substantial agreement with the experimental data available at that time.

Recent precise measurements of the critical fields of a number of superconductors incident to the investigation of the isotope effect[27,33,34] have confirmed that the parabolic relation is not an accurate representation of the threshold field curve for most superconductors. Prompted by the results of these measurements, Marcus and Maxwell[35] re-examined the assumptions on which the two fluid model is based. They have shown that a much better description of the experimental results can be obtained if the parameter α in the form of $K(\omega)$ chosen by Gorter and Casimir is not fixed at $\frac{1}{2}$ but is allowed to vary from one metal to another. This form for $K(\omega)$ is called the α model. Values of α ranging from 0.38 to 0.55 have been found among the superconductors investigated.[27] Furthermore, if $K(\omega)$ is taken to be independent of the isotopic mass then the two fluid model also exhibits the experimentally observed property that the threshold field curve for each superconductor is independent of the isotopic mass when it is expressed in terms of the reduced field $h=H/H_0$ and the reduced temperature $t=T/T_0$. Expressing the heat capacity in reduced terms, the α-model gives the following expression for the electronic heat capacity in the superconducting phase:

$$c/t=C_s^{\mathrm{el}}/\gamma T=(1+\alpha)/(1-\alpha)t^{(2\alpha/1-\alpha)}. \tag{11}$$

C_s^{el} is the electronic contribution to the heat capacity in the superconducting phase, and γT is the normal electronic heat capacity.

In 1947, Koppe[36] calculated $K(\omega)$ by making an explicit assumption for the effect of the onset of superconductivity on the distribution in energy of the free electrons in the normal phase. Prompted by the Heisenberg theory of superconductivity[37] he assumed that a fraction ω of all momentum states with energies above ϵ_0, the Fermi energy at absolute zero, are not available to the normal electrons after the condensation has begun. $K(\omega)$ is obtained by modifying the distribution in energy by the factor $(1-\omega)$ for energies above ϵ_0 and evaluating the integrals for the total number of electrons and the total energy by the method of Sommerfeld and Bethe.[38] The result is an expression which cannot be given in simple form. Representative values for the electronic heat capacity given by this function have been tabulated by Brown, Zemansky, and Boorse.[7]

Since these calculations are concerned only with the electronic heat capacity, the lattice heat capacity must be subtracted from the measured values. This

[31] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **96**, 1442 (1954).
[32] C. J. Gorter and H. B. G. Casimir, Physik. Z. **35**, 963 (1934).
[33] Serin, Reynolds, and Lohman, Phys. Rev. **86**, 162 (1952).
[34] E. Maxwell, Phys. Rev. **86**, 235 (1952).
[35] P. M. Marcus and E. Maxwell, Phys. Rev. **91**, 1035 (1953).
[36] H. Koppe, Ann. Physik **1**, 405 (1947).
[37] W. Heisenberg, Z. Naturforsch. **2a**, 185 (1947).
[38] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. **24**, Part 2.

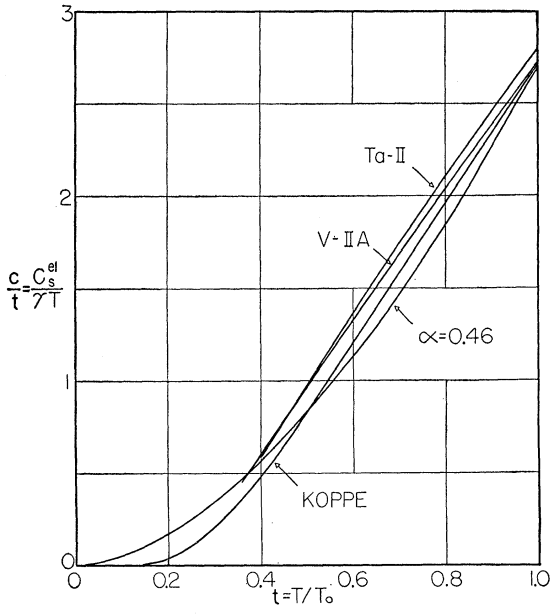

FIG. 9. The reduced electronic heat capacities of vanadium and tantalum in the superconducting phase plotted as c/t *versus* t. The values predicted by Koppe's theory and the α model ($\alpha=0.46$) are also shown.

can be done if it is assumed that the lattice contribution is unaffected by the transition to superconductivity. Then the electronic heat capacity in the superconducting phase is given by the equation

$$C_s^{el}=C_s-(464/\Theta^3)T^3. \tag{12}$$

The results for samples V–IIA and Ta–II, expressed in terms of the reduced temperature and the reduced heat capacity, are shown in Fig. 9. $c/t(=C_s^{el}/\gamma T)$ has been plotted against t since it was found that the relation given by Koppe is very nearly linear above $t=0.4$ on this plot. The curve representing the α model corresponds to the value $\alpha=0.46$. This value was chosen to fit the results for vanadium at $t=1$. Other values for α do not improve the agreement with the experimental results.

Considering the simple assumption on which Koppe's calculation is based, the agreement with the experimental results for V–IIA and Ta–II is rather striking. The measurements of Corak, Goodman, Satterthwaite, and Wexler[31] extend the results on vanadium down to $t=0.23$. These data cross the Koppe curve at $t=0.3$ and lie slightly below it at lower t. This behavior is similar to that observed for niobium,[7] although the departure from the Koppe curve is somewhat greater in this case. Although the results for tantalum and vanadium are in close agreement, those obtained for niobium indicate that the heat capacity when expressed in reduced form is not a universal function and that the primary defect of Koppe's calculation is that it predicts the same reduced heat capacity, as well as the same reduced threshold field curve, for all superconductors. The α model does possess the added flexibility of an adjustable parameter, however the agreement with the calorimetric data for tantalum and vanadium is not as good as for the Koppe model.

The magnetic measurements agree with the calorimetric measurements in so far as they show that the reduced threshold field curve is not a universal function for all superconductors. Consequently the α-model with its adjustable parameter does give a somewhat better description of many of the experimental results than does the Koppe calculation. There is evidence to show that both models represent a considerable improvement over the simple cubic heat capacity and the parabolic threshold field curve, but the models must be refined if there is to be agreement in detail with the experimental results.

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