# Superconducting Critical Field of Tantalum as a Function of Temperature and Pressure*

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The results of precise critical field measurements on tantalum samples which show "soft" superconducting behavior are given along with direct measurements of the pressure effect, $(\partial H_c/\partial P)_T$, as a function of temperature. The Bardeen-Cooper-Schrieffer theory is used as a guide in the extrapolation of these data to absolute zero from 1.1°K. The advantages of using an $H^2$ vs $T^2$ representation for both the critical-field and pressure-effect data are discussed, and it is shown that if both sets of data can be represented in terms of power series [$H^2$ or $(\partial H_c^2/\partial P)_T$ vs $T^2$] over a limited range of temperature, it is then possible to write down explicit power series expressions for the differences in the thermodynamic functions between the normal and superconducting states over this same temperature range. The electronic contributions to the specific heats and the thermal expansions for tantalum are calculated from the experimental data.

## I. INTRODUCTION

TANTALUM has been classified in the past as a hard superconductor because of superconducting transitions that were quite broad and which displayed irreversible behavior. In recent years, however, a series of investigations has shown that tantalum can be made to exhibit soft superconducting behavior if high-purity metal is degassed near its melting point in vacuums of the order of $10^{-9}$ mm Hg or better.[1–4] The investigations which are described below were made possible by the use of these techniques to prepare the samples.

The initial purpose in undertaking the present study was to investigate the discrepancies between direct measurements of the change in zero-field transition temperature with pressure,[5] and those measurements in which the same quantity was deduced from critical-field pressure-effect data,[6] or the change in length of a sample at the transition in a magnetic field.[7] It was possible that the discrepancies were due to a lack of reversible behavior of the samples in a magnetic field, so every effort was made in the present work to produce samples of tantalum which were of sufficient purity so as to exhibit virtually ideal magnetic transitions. Two separate measurements on the same samples were involved; first, a precise determination of the critical-field curve at zero pressure, and second, the change in this critical field with 2000-atm pressure for various temperatures. The high pressure was generated using solid helium, with every indication that no pressure gradients existed.

The major interest in obtaining critical-field data as a function of temperature and pressure (or volume) arises because these data, if sufficiently precise, can be used to obtain a complete picture of the electronic contribution to the entropy and specific heat,[8] as well as to the thermal expansions, for both the normal and superconducting states.[9] For many substances (although not for tantalum), the lattice contributions are so large as to make direct determinations of these quantities impossible, and the superconducting measurements form the only practical method for evaluating these electronic contributions to the thermodynamic functions. In order to obtain absolute values, however, the assumption must be made that the lattice contributions do not change at the superconducting transition; if they do, one can calculate only differences in thermodynamic properties between the two states.

## II. EXPERIMENTAL DETAILS

### A. Zero-Field Work

Initial experiments were made using a sample of highly degassed tantalum wire which was kindly furnished by Dr. J. I. Budnick of the IBM Laboratories.[10] In order to compare data on this wire with earlier results, its zero-field transition temperature $T_c$ was measured as a function of pressure to 10 000 atm in the apparatus described by Jennings and Swenson.[5] This sample (0.5 mm diameter, 2 in. long) was waxed to a brass plate, and cut into small segments (roughly 20 pieces, each 2.5 mm long). These then were mounted on end parallel to the axis of the high-pressure cylinder, and were separated by at least a diameter by a piece of cellophane tape. The actual data (Fig. 1) showed no evidence of sample deformation or pressure gradients, and the sharpness of the transitions (less than $10^{-3}$ deg) is indicative of the purity of the samples, as is the zero field, zero-pressure transition temperature, 4.482 (±0.001)°K. When the sample holder was warmed to

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[1] W. B. Ittner and J. F. Marchand, Phys. Rev. **114**, 1268 (1959).
[2] D. P. Seraphim and R. A. Connell, Phys. Rev. **116**, 606 (1959).
[3] J. I. Budnick, Phys. Rev. **119**, 1578 (1960).
[4] D. P. Seraphim, J. I. Budnick, and W. B. Ittner, Trans. Am. Inst. Mining Met. Engrs. (to be published).
[5] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).
[6] M. D. Fiske, J. Phys. Chem. Solids **2**, 191 (1957).
[7] J. L. Olsen and H. Rohrer, Helv. Phys. Acta **30**, 49 (1957). See also a recent summary by the same authors, *ibid.* **33**, 872 (1960).
[8] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), 2nd ed., Chap. 3.
[9] P. G. Klemens, Phys. Rev. **120**, 843 (1960).
[10] The authors are indebted to Dr. J. I. Budnick of the IBM Laboratories for supplying us with this wire.

room temperature after this run, there was no evidence of deformation of the samples, and indeed, the individual wires were still standing on end with the tape unbroken.

### B. Critical-Field Measurements

The samples used in the critical-field work were made in this laboratory from a high-purity electron-beam melted wire, 0.8 mm diameter, which was kindly furnished by the National Research Corporation.[11] Three separate samples were prepared by electron-bombardment heating of pieces of this wire to 2900°C in a vacuum of better than $10^{-9}$ mm Hg. An all-glass vacuum system which used a mercury diffusion pump, a liquid-nitrogen trap and an oven for outgassing of the glass at 500°C was used. The resulting samples showed grains about 1.5 mm long, and had residual resistivity ratios $[\rho(300)/\rho(0)]$ in the normal state of 1500 ($\pm$500), the uncertainty being due to the short lengths available (1.5 in.) and the extreme danger of introducing strains and inhomogeneities by deforming the soft wires in handling. This ratio was of the same order as that reported by the IBM workers for wires of this size.[1-4] Samples 1.0 cm long (two from each wire prepared) were cut by waxing the wires to a brass bar, and then using a milling cutter rotating at a high speed.

The critical-field measurements, both at zero pressure and as a function of pressure, were made in a 2.5-liter capacity all-metal liquid helium Dewar, with a liquid nitrogen-cooled solenoid mounted about its lower end. The solenoid was 8 in. long, with a center opening of roughly 2-in. diameter. Because of the exacting needs of the $H_c$ vs $T$ measurements, it was necessary to have an axial field homogeneity of 0.01% over roughly one inch in the center of the solenoid. This was accomplished by means of compensating coils, and the homogeneity was verified both by a mutual inductance probe and by nuclear magnetic resonance measurements. The calibration of the solenoid was 101.54 ($\pm$0.02) gauss/amp, as determined from the proton resonance, and was found to be independent of field from 600 to 1200 gauss.[12] Helmholtz coils were used to reduce the effect of the earth's field to a few hundredths of a gauss.

The solenoid current was furnished by submarine batteries (20 v), and was regulated and held constant through the use of a transistorized current regulator.[13] Critical-field work of the type described below requires the ability to increase the current rapidly and smoothly to just below the critical field, and then to be able to vary the current in infinitesimal steps while passing through the transition. Transistors allow this to be done very easily.

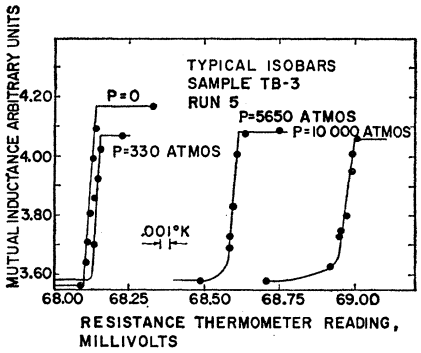


FIG. 1. Typical experimental data for the zero-field, high-pressure experiments.

All of the superconducting transitions were observed using a 33-cps mutual-inductance technique and a Hartshorn bridge. The excess paramagnetism of the intermediate state always was observed,[14] giving a unique criterion for determining the transition field. The ac measuring fields of roughly 0.1 gauss, rms, were used, and it was verified that there was no dependence of the critical field on measuring field for wide variations about this amplitude.

In the measurements which are described below, the temperatures were determined from a vapor-pressure bulb mounted near the sample, and calculated from the $T_{55E}$ scale. The constancy of the temperature was monitored using the resistance of a 51-ohm (nominal) Allen Bradley resistor, also mounted near the sample. The potential drop across this resistor for a fixed current was measured on a Rubicon type B potentiometer, with a 0–100 $\mu$v recording potentiometer across the galvanometer terminals giving a continuous record of temperature fluctuations. This system and the vapor-pressure control system were identical with that used in previous work.[5]

The zero-pressure critical-field apparatus and techniques will not be described in detail, since the methods were identical with those used in the pressure work, and the apparatus was much less complex. Above the $\lambda$ point a vapor-pressure bulb was used, while below this temperature a $\frac{1}{4}$-in. open tube, ending just above the liquid surface, was used to read the vapor pressure over the bath. The temperature determinations were much more difficult in the high-pressure apparatus due to thermomolecular effects; and while this did not affect the $(\partial H_c/\partial P)_T$ results, less precise absolute values of the temperature resulted at the lowest temperatures attained with this apparatus. Hence, zero-pressure critical fields as determined in the pressure runs are not given.

[11] The authors are indebted to the National Research Corporation of Cambridge, Massachusetts, for making this wire available.

[12] The solenoid calibration was done by R. A. Hultsch of the Ames Laboratory, and appreciation is expressed for the assistance which was given.

[13] The regulator was of the type described by Garwin, Hutchinson, Penman, and Schapiro, Rev. Sci. Instr. **30**, 105 (1959), and was designed and constructed in the Ames Laboratory Instrumentation Shop.

[14] D. Shoenberg, Proc. Cambridge Phil. Soc. **33**, 559 (1937).

### C. High-Pressure Work

Previous work on the change in the zero-field transition temperature of tantalum with pressure[5] indicated that $(\partial H_c/\partial P)_T$ would be roughly $-10^{-3}$ gauss/atm, or a 2 gauss decrease in 2000 atm. This corresponds to a variation in temperature at constant pressure of about $6\times10^{-3}$ deg at low fields, and to roughly 0.2% of the highest critical fields. Thus, to be able to measure such a small effect, either a very precise temperature measuring technique must be used (accurate and reproducible to $10^{-4}$ deg from day to day), or a differential technique utilized in which the absolute temperature is relatively unimportant. The latter method was chosen for these experiments, and the difference in the critical fields of a sample under 2000-atm pressure and a second identical sample (cut from the same wire) at zero pressure was measured, with (as was described above) the zero-pressure critical-field curve being determined in a separate experiment.

The brute-force technique which was used in previous zero-field experiments[5] to 10 000 atm was not used for two reasons. First, the pressures generated by the solid hydrogen were not truly hydrostatic, and it was hoped to eliminate this as a factor. Second, because of the hydraulic press, the evaporation rates of liquid helium from the Dewar vessel were very large, and the necessary temperatures near 1°K would be difficult to obtain. The method which was used to apply the pressure was an adaptation of a method described by Dugdale and Hulbert,[15] in which fluid helium in a bomb was frozen around the sample at constant volume. In the present experiments, the helium was frozen at constant pressure, since slightly higher final pressures could be obtained for a given fluid pressure. The previous evidence[15,16] and our experience indicate that the pressures which were generated were truly hydrostatic. An air-driven oil pump provided a convenient means of attaining the maximum pressure of 2000 atm which was used for the measurements. The helium gas was compressed in a conventional oil-mercury-gas system, which will not be described.

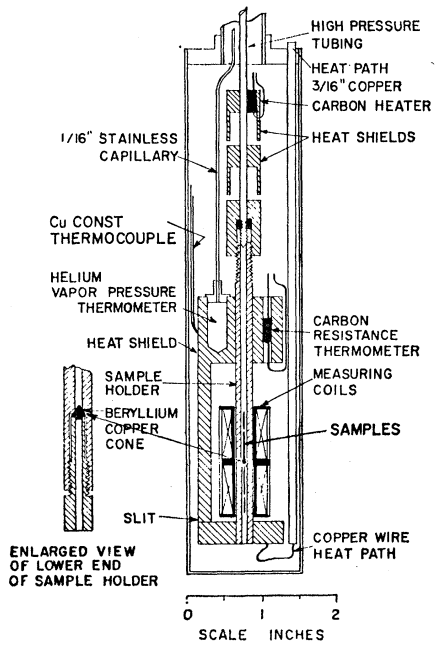


FIG. 2. The high-pressure sample holder. The surrounding liquid helium Dewar and the liquid-nitrogen-cooled solenoid are not shown.

Two separate and conflicting requirements had to be be met in the high-pressure sample holder. First, the helium had to be solidified around the sample at constant pressure, which necessitated the cooling of the sample holder from the opposite end from the filling tube, while maintaining a temperature gradient along it. Second, once the helium was solidified, temperature differences of more than $10^{-4}$ deg could not be allowed between the two samples. These conflicting requirements were met with the sample holder shown in Fig. 2. The high-pressure bomb ($\frac{1}{4}$ in. o.d., $\frac{1}{16}$ in. i.d., 3 in. long, constructed from hardened beryllium copper) was enclosed in a vacuum jacket which extended to room temperature with a heat station in the Dewar neck. The lower end of the bomb was connected to liquid-helium temperatures by means of a copper wire, so that with a vacuum in the jacket and the bomb initially at 77°K, the bomb could cool slowly through the melting line, the helium solidifying from the bottom upwards at constant pressure until the filling line ($\frac{1}{8}$-in. o.d. hard-drawn stainless steel, 0.024-in. hole filled with a 0.020-in. stainless steel wire) was blocked. Exchange gas at about 7 mm Hg pressure was then admitted to the vacuum jacket, which, together with the heat shields, reduced the heat leak into the bomb, while the copper block reduced the temperature difference across the bomb to a negligible value. The slit in the copper block which is shown in Fig. 2 offered a large impedance to heat flow down the block when the vacuum chamber was evacuated, but effectively became a good conductor of heat with exchange gas present.

The amount of exchange gas seemed to be quite critical. If too much (greater than 1 cm Hg pressure) were present, large temperature fluctuations of the bomb occurred, and a large heat leak was observed into the helium Dewar. These dropped rapidly as the exchange gas pressure was lowered below 1 cm; the apparatus was usually operated at a helium pressure of 7 mm Hg or lower in the vacuum jacket.

The lack of significant (less than $10^{-4}$ deg) temperature differences between the two samples was verified in several ways. First, a preliminary experiment with vapor-pressure thermometers on opposite ends of the bomb indicated that the temperature difference was

[15] J. S. Dugdale and J. A. Hulbert, Can. J. Phys. **35**, 720 (1957).

[16] J. S. Dugdale and D. Gugan, Proc. Roy. Soc. (London) **A241**, 397 (1957).

this small; after this experiment better heat shields and the copper block were added, which should have reduced the difference still further. Runs made at constant temperature showed that within experimental error, $\Delta H$ was a linear function of pressure, the $\Delta H$ vs $P$ curve passing through the origin. Finally, the agreement with the zero-field results at $T_c$ was excellent, these latter being obtained in a different apparatus and using a different technique.

The determination of the pressure is a major problem in all high-pressure experiments at low temperature. In the present experiments, the freezing pressure (and temperature) was known, and the results of Dugdale and Simon[17] could be used to calculate the change in pressure in the solid helium due to cooling at constant volume from the melting line to 4°K. This correction was of the order of 5%. In order to verify that the helium actually had solidified at constant pressure, a check on the internal helium pressure was obtained by using the difference near $T_c$ in the critical fields of two identical single-crystal tin samples, one under pressure and the other at zero pressure (the second set of samples shown in Fig. 2). The data of reference 5 were assumed to be correct, and a pressure was calculated. The two pressures always were identical to within a few percent, a comforting observation which indicated that the two sets of experiments are consistent.

Figure 3 illustrates the data which were obtained in a typical pressure run. The secondaries of the measuring coils (each 750 turns) in Fig. 3 were wound in opposition, with a common primary (10 turns/cm). Thus, as the magnetic field was increased, first a mutual inductance contribution due to the sample under pressure appeared, then the contribution due to the zero-pressure sample. The hump is due to the apparent paramagnetism of the intermediate state, and the width of the hump is several times greater than would be expected on the basis of the calculated demagnetization factor. Because of the small skin depth even at 33 cps, the whole sample was not observed, only the outer 0.1 mm; this is probably why these curves do not show the very large magnitude of the susceptibility which would be expected ideally in the intermediate state.

The abrupt change in the mutual inductance was taken as the transition. The off-balance signal exhibited a great deal of noise and jitter in the intermediate state, which completely disappeared in the normal state. By observing the temperature and pressure dependence of the initial drop in the mutual inductance of the high-pressure sample (left-hand side, Fig. 3), this was shown to be characteristic of the intermediate state, with the true superconducting transition being given by the second drop. When necessary, the critical fields were corrected for any temperature drifts which occurred in the time between the observations of the two transitions.

[17] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

TABLE I. The experimental data for the zero-pressure critical-field curve of tantalum.

| Ta-10 | | Ta-11 | |
|---|---|---|---|
| T (°K) | $H_c$ (gauss) | T (°K) | $H_c$ (gauss) |
| 4.196 | 91.73 | 4.476 | 1.52 |
| 3.750 | 227.21 | 4.460 | 6.87 |
| 3.511 | 295.64 | 4.324 | 51.11 |
| 3.017 | 426.30 | 4.200 | 91.60 |
| 2.609 | 522.70 | 4.021 | 146.52 |
| 2.173 | 614.23 | 3.757 | 225.59 |
| 2.000 | 645.9 | 3.456 | 311.45 |
| 1.804 | 679.4 | 2.672 | 507.9 |
| 1.615 | 708.3 | 2.000 | 645.7 |
| 1.422 | 734.3 | 1.732 | 689.7 |
| 1.141 | 766.8 | 1.422 | 732.5 |
| 1.112 | 769.8 | 1.121 | 767.4 |

## III. EXPERIMENTAL RESULTS

The experimental critical-field data for runs on two different samples are given in Table I. The deviation plot of Fig. 4 (which shows the difference between the observed critical-field curve and an assumed parabolic shape) illustrates the amount of scatter in the data. A systematic difference in the critical field values seems to exist below 1.5°K, with a mean discrepancy of about one gauss. This is not understood. The critical-field data as a whole could be represented with an rms deviation of 0.55 gauss and a maximum deviation of 1 gauss, by the expression

$$H=825.3-45.25\,T^2+0.01859\,T^4+0.02000\,T^6 -5.312\,T^8, \quad (1)$$

$$1.1°<T\leq 4.479°\text{K}=T_c.$$

The rms deviation (0.55 gauss) is equivalent to an uncertainty in the temperature of $0.5\times10^{-3}$ deg near $T_c$, and to an uncertainty of less than 0.1% in the critical field near 1.1°K. The actual data agree very well as to shape of the critical-field curve when compared with data given by Budnick[3] and Mapother *et al.*[18] but a

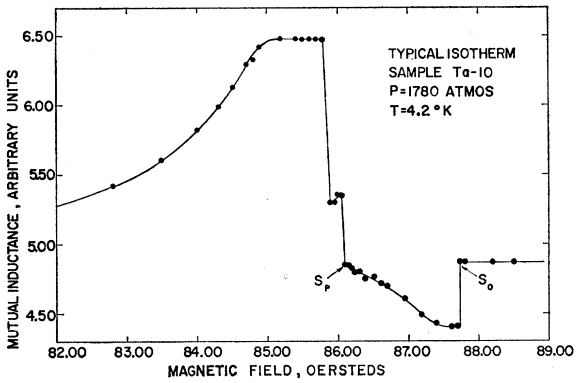


FIG. 3. A typical set of experimental data for a pressure-effect run. The transition fields of the high-pressure sample $S_p$ and the zero-pressure sample $S_0$ are indicated. The reason for the different magnitudes of the humps is not known.

[18] R. W. Shaw, D. E. Mapother and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

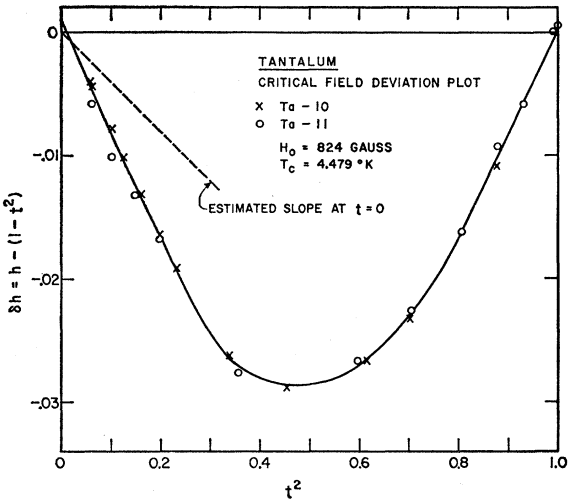


FIG. 4. The experimental zero-pressure critical-field data, expressed as a deviation from a critical-field curve of parabolic behavior. An $H_0=824.0$ gauss has been assumed, and the solid curve corresponds to Eq. (1).

systematic discrepancy seems to exist in the absolute values, our data being slightly lower. Shaw has used the apparatus of reference 18 to determine six points on the low-temperature end of the critical-field curve of sample Ta-11 and finds that $H_0=828$ gauss (compared with 825 gauss above), with excellent agreement as regards the shape of the curve. It was his impression that the transitions for this sample were, if anything, better than were observed with their sample of IBM tantalum.[19] Sample Ta-11 gave the higher critical fields in the present measurements (Table I), so that the magnitude of the systematic discrepancy between the two different techniques is perhaps of the order of 0.2%.

The results of the zero-field experiment which used solid hydrogen as a pressure transition to 10 000 atm are given in Fig. 5. The value of $dT_c/dP$ which can be obtained from these data $[dT_c/dP=-2.6(\pm0.1)\times10^{-6}$ deg/atm] is in excellent agreement with other data on considerably less pure tantalum (the $T_c$'s being as low as 4.30°K, compared with the present 4.47°K).[20]

The data for the change in critical field with pressure, $(\partial H_c/\partial P)_T$, as obtained in several runs with two different sets of samples, are given in Fig. 6. The uncertainties at lower temperatures are due to difficulties associated with the finite width of the transitions (several times the shift which was observed), possible inhomogeneities in the magnetic fields (0.01% represents about 0.08 gauss near 1°K) and excessive bridge noise caused by vibrational pickup in the mutual inductance coils. For purposes of calculation (see the next section), it is convenient to use the quantity $(\partial H_c^2/\partial P)_T$, and the data of Fig. 6 can be represented by the expression

$$(\partial H_c^2/\partial P)_T=-1.7(\pm0.2)[1-1.1(\pm0.12)t^2+0.10(\pm0.12)t^4], \quad (2)$$

where $t=T/T_c$ is the reduced temperature. This expression (in which like signs must be taken together) reflects the relatively higher accuracy of the data taken near $T_c$, and the uncertainties in the low-temperature data.

## IV. THERMODYNAMIC CALCULATIONS

The major use of the data given in Sec. III is to calculate the electronic contributions to the various thermodynamic functions for tantalum. It has been customary to use an $H$ vs $T^2$ power-series representation of the data to do this, but the calculations become somewhat tedious as various derivatives are evaluated.[8] However, it will be shown below that if an $H^2$ vs $T^2$ power-series representation is used, the calculations become much less involved, and it is possible to write down explicit expressions for both the heat capacity and the thermal expansion due to the electrons in the superconducting state. The major disadvantage is that, while the $H$ vs $T^2$ is almost linear (due to the approximately parabolic nature of the critical field curves), $H^2$ varies rapidly with $T^2$, and near $T_c$ the representation is not precise. The consequences of using this latter representation are discussed in some detail below, and the analysis is applied to the specific case of tantalum.

The thermodynamic relationship on which the following analysis is based,

$$(\partial H_c/\partial T)_P=-(4\pi/V_sH_c)(S_n^{el}-S_s^{el}), \quad (3)$$

is derived elsewhere.[8] Here it has been assumed that the lattice properties do not change in the superconducting to normal transition. This is a reasonable assumption since the compressibilities in the two states are the same to within at least one part in $10^5$. All available experimental data for pure metals in the normal state indicate a free electron-type behavior, with $C_n^{el}=S_n^{el}=\gamma T$.[21] With this assumption, Eq. (3) can be rewritten as

$$(\partial H_c^2/\partial T^2)_P=-(4\pi/V_s)(\gamma-T^{-1}S_s^{el}). \quad (4)$$

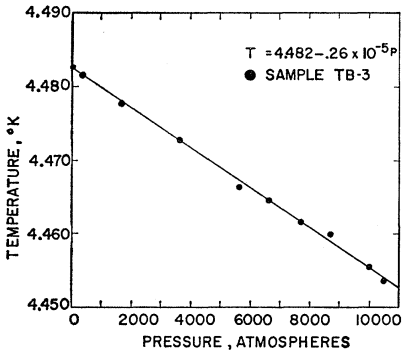


FIG. 5. The results for the zero-field, high-pressure experiment. The relative accuracy of the experimental points ($10^{-4}$ deg) is much higher than the absolute accuracy ($10^{-3}$ deg).

[19] R. W. Shaw (private communication, 1960).
[20] See reference 5, and unpublished data from this laboratory.
[21] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, New York, 1956), 2nd ed., Chap. 10.

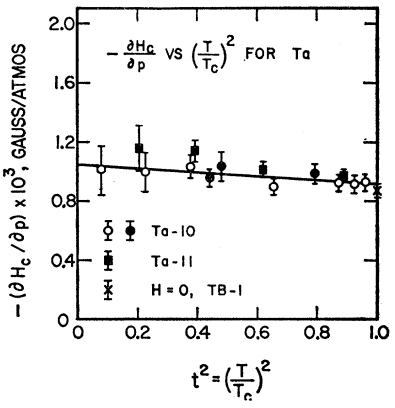


FIG. 6. The $(\partial H_c/\partial P)_T$ experimental results.

On theoretical grounds, it has been shown that $S_s^{el}$ should decrease rapidly as the temperature approaches zero,[22] and most experimental evidence indicates that $S_s^{el}$ varies at least as rapidly as $T^3$ in the low temperature limit. In this limit, then, $S_s^{el}$ is negligible compared with $S_n^{el}$, and Eq. (4) can be integrated to give

$$H^2=H_0^2-(4\pi\gamma/V_s)T^2,$$

or

$$h^2=1-(4\pi\gamma T_c^2/H_0^2V_s)t^2, \quad (5)$$

where $H_0$ is the critical field at absolute zero, $T_c$ is the zero-field transition temperature, and $h=(H/H_0)$ and $t=(T/T_c)$ are reduced critical fields and temperatures, respectively.

Equation (5) indicates one immediate advantage of an $H^2$ vs $T^2$ plot, since data when plotted in this manner should approach linear behavior with decreasing temperature much sooner than when $H$ is plotted vs $T^2$. It was for this reason that we initially chose to represent our data in terms of $H^2$ (or $h^2$) vs $T^2$ (or $t^2$), even though a better fit was obtained with the $H$ vs $T^2$ power series [Eq. (1)]. One could, indeed, merely square this expression, but it would become quite unmanageable in length. The choice of an $H^2$ representation, either in terms of $T$ or $T^2$, is obvious from a consideration of the basic thermodynamic relationship for the free-energy difference between the two states at the transition line.[8]

The difference between the heat capacities of the normal and superconducting states can be obtained from Eq. (4) by differentiation:

$$C_n^{el}-C_s^{el}=-(V_sT/4\pi)\{(\partial H_c^2/\partial T^2)+2T^2[\partial^2(H_c^2)/\partial(T_c^2)^2]\}. \quad (6)$$

Since $C_n^{el}$ is given directly by the low-temperature portion of the critical-field curve [Eq. (5)], this equation can be used to calculate $C_s^{el}$ explicitly.

Equation (5) also can be used to establish the low-temperature behavior of the pressure-effect data, since in this limit,

$$\lim_{T\to 0}(\partial H_c^2/\partial P)_T=(dH_0^2/dP)+(4\pi k_s\gamma/V)[(d\ln\gamma/d\ln V)-1]T^2, \quad (7)$$

where $k_s=(-\partial\ln V/\partial P)_T$ is the isothermal compressibility. This expression shows how pressure effect data may be used to obtain the volume dependence of $\gamma$, and, hence, of the density of states.[7] This quantity is of some theoretical importance, but it also is of interest since it affords a means for estimating the electronic contribution to the thermal expansion of the normal state. If it is assumed that the entropy of the normal metal can be expressed as the sum of an electronic term $(S_n^{el}=\gamma T)$ and others, the Maxwell relationship, $(\partial V/\partial T)_P=-(\partial S/\partial P)_T$, can be used to obtain

$$\beta_n^{el}=(\partial\ln V_n/\partial T)_P=(k_n\gamma T/V)(d\ln\gamma/d\ln V). \quad (8)$$

In all future expressions, the difference between the volumes and the compressibilities of the two states will be ignored as negligible.

Finally, a differentiation of Eq. (3) with respect to pressure, together with the use of the same Maxwell relationship, gives the difference between the thermal expansions of the normal and superconducting states:

$$\beta_n^{el}-\beta_s^{el}=(T/4\pi)\{\partial/\partial T^2(\partial H_c^2/\partial P)_T-k[\partial^2H_c^2/\partial(T^2)^2]_P\}. \quad (9)$$

The second term is a magnetostriction contribution which arises because Eq. (3) applies only along the equilibrium line. Equations (8) and (9) can be combined to give explicitly the electronic thermal expansion of the superconducting state in the case where only the electronic thermodynamic functions change at the transition.

The above discussion is quite general, and involves a restatement of conventional thermodynamic expressions. When analyzing experimental data, however, it is useful to have an indication as to the expected temperature dependence of $h^2$. In particular, it is desirable to have some guide as to the temperature below which a linear dependence of $h^2$ on $t^2$ may be expected to occur, since most data do not extend to sufficiently low temperatures. Bardeen, Copper, and Schrieffer have used a simplified model of a superconductor to predict a generalized critical-field curve which can be expressed in reduced terms, and from it, they have calculated the thermodynamic properties of the electrons in the superconducting state.[22] Their results can be used to give an approximate indication of the behavior of an actual critical-field curve.[23] Their Eq. (3.38) for the critical-field curve has been evaluated using numerical integrations by a digital computer where necessary, and

[22] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957); referred to here as BCS. See also B. Muhlschlegel, Z. Physik **155**, 313 (1959).

[23] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957). A variation of this approach to obtain $\gamma$ from critical-field data was used. Equations (5) were given also by B. Serin in C. J. Gorter, *Progress in Low Temperature Physics, Vol. 1* (Interscience Publishers, Inc., New York, 1955), p. 138.

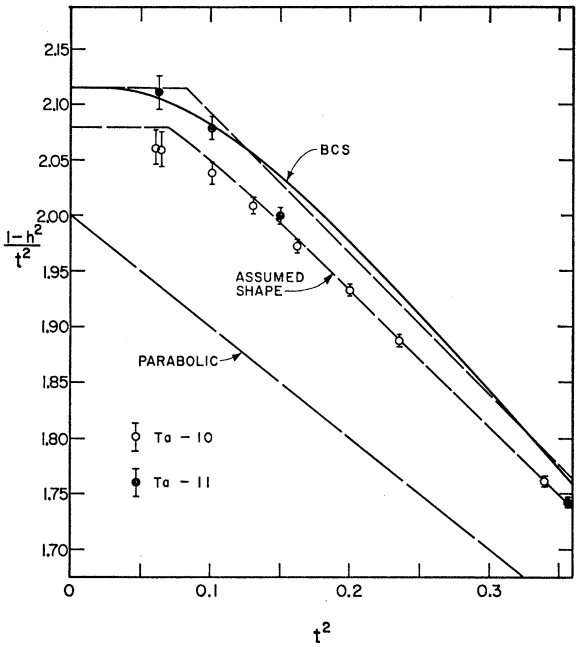


FIG. 7. A reduced critical field plot of the form, $(1-h^2)/t^2$ vs $t^2$. The error bars represent $\pm 0.05\%$ uncertainty in the data.

the low-temperature part of the resulting curve has been plotted in Fig. 7.[24] The particular representation $[(1-h^2)/t^2$ vs $t^2]$ was chosen because the expected low-temperature behavior of $h^2$ results in an asymptotic approach of the ordinate to the value 2.1148 as the temperature approaches zero. This plot is also extremely sensitive to uncertainties in both $h$ and $t$ in the region of interest ($t^2 \leq 0.3$), the effect of $\pm 0.05\%$ variations in $h$ are represented by the error bars on the experimental points. It also can be shown that a linear (nonhorizontal) curve on the graph corresponds to a $T^4$ contribution to the free energy (and, hence a $T^3$ contribution to the heat capacity) of the superconducting state in the region of linearity.

The theoretical curve in Fig. 7 can be used in the analysis of the critical-field data as follows. Within our experimental accuracy, from $t^2=0.1$ to $t^2=0.3$ the theoretical curve would appear to be indistinguishable from a power series representation which included only $t^2$ and $t^4$ terms, and, hence, it would be possible to replace the BCS curve on this plot below $t^2=0.3$ (within $0.05\%$ in $h$) by two straight lines which intersect at roughly $t^2=0.08$, as is suggested by the dashed lines in Fig. 7. Only extremely precise experimental data could hope to yield the shape of the critical-field curve below $t^2=0.1$, and uncertainties in the temperature scale below 1°K could mask this completely.

The limiting values for both $H_0$ and $\gamma$ were calculated from our tantalum data in the following manner. A power-series representation of the experimental data below $t^2=0.34$ (of the form $H^2=H_0'^2+A_2T^2+A_4T^4$) was used to calculate $(\partial H_c^2/\partial T^2)_P$ at $T^2=0.08T_c^2$ (1.14°K), and this slope was used to obtain a linear extrapolation of the data from this point to absolute zero. This extrapolation corresponds with the horizontal part of the theoretical curve in Fig. 7, and can be used to give a value both for $H_0$ and for $\gamma$. The power series (which effectively assumes a $T^3$ dependence of the heat capacity to absolute zero) also can be used to calculate a second set of values for these two quantities, and, presumably, the correct values lie somewhere within these limits. When this procedure was carried out for tantalum, both $H_0$ and $\gamma$ were smaller for the linear extrapolation than for the quadratic extrapolation, the two values for $H_0$ differing by about 3 gauss ($0.4\%$), while $\gamma$ decreased from $15.3\times10^{-4}$ cal/mole-deg$^2$ to $13.8\times10^{-4}$ cal/mole-deg$^2$, or by $10\%$.

In order to calculate the thermodynamic functions for the superconducting state, it is convenient to have the experimental data expressed in terms of the reduced variables, $h$ and $t$, in the form:

$$h^2=\sum_{n=0}^{N} a_{2n}t^{2n}. \tag{10}$$

Using $H_0=824$ ($\pm 1.5$) gauss, which corresponds with a value for $\gamma=14.3(\pm 0.5)\times10^{-4}$ cal/mole-deg$^2$, the experimental data for tantalum could be expressed as

$$(0.06<t^2<0.34)\ h^2=1.0017-2.19140t^2+1.25219t^4, \tag{11a}$$
$$\text{rms dev.} = 0.65 \text{ gauss};$$

$$(0.06<t^2<0.88)\ h^2=1.0054-2.2525t^2+1.4967t^4-2.4970t^6, \tag{11b}$$
$$\text{rms dev.} = 0.75 \text{ gauss}.$$

The maximum value of $t^2$ was introduced because the least-squares fits were very insensitive to errors for small values of $h^2$. A major contribution to the deviations is given by the systematic differences between the samples below 1.5°K.

The most probable value of $\gamma=14.3$ $(\pm 0.5)\times10^{-4}$ cal/mole-deg$^2$ which can be obtained from these measurements is in essential agreement with the calorimetric value of $13.6\times10^{-4}$ cal/mole-deg$^2$ which is given by White, Chou, and Johnston,[25] the same molar volume being used in each case ($V_m=10.83$ cc). Both the deviation plot (Fig. 4) and the representation of the data in Fig. 7 are sensitive to the choice of $H_0$, and, hence, to $\gamma$, since these are closely related. It is convenient to define a new quantity

$$a_2'=-\gamma(T_c/H_0)^2 4\pi/V=-2.08, \tag{12}$$

which is, essentially, the limiting slope of the "true" $h^2$ vs $t^2$ plot at absolute zero; $a_2'$ is then the asymptotic

[24] To be published in an Iowa State University report. A further discussion will be given in a paper by J. E. Schirber and C. A. Swenson, following paper [Phys. Rev. **123**, 1115 (1961)].

[25] D. White, C. Chou and H. L. Johnston, Phys. Rev. **109**, 797 (1958). This paper gives references to work published earlier.

low-temperature ordinate of the plot in Fig. 7 [where Eq. (11a) is also plotted], and $(a_2'/2-1)$ is the limiting slope of the deviation plot of Fig. 4. One advantage of the $h^2$ vs $t^2$ representation is immediately obvious; the $h$ vs $t^2$ plot, although apparently linear below $t^2=0.34$ due to a predominantly $T^3$ contribution to its heat capacity, reaches a true linear behavior for tantalum only below $t^2=0.02$ (0.6°K). The $h^2$ vs $t^2$ curve, on the other hand, should become linear below roughly $t^2=0.05$ (1°K).

The heat capacity of the superconducting state ($C_s^{el}$) can be obtained from Eq. (6), and, in the notation of Eq. (10),

$$C_s^{el}/\gamma T_c=-[(a_2-a_2')/a_2']t-6(a_4/a_2')t^3 \times[1+2.5(a_6/a_4)t^2+4.67(a_8/a_4)t^4], \quad (13)$$

$$=-0.053t+3.62t^3, \quad (0.06<t^2<0.34); \quad (13a)$$

$$=-0.080t+4.32t^3(1-0.416t^2), \quad (0.06<t^2<0.88). \quad (13b)$$

These expressions are limited to the region of validity of the power series (11a), (11b) from which they are calculated, and cannot be used for extrapolation at either temperature limit. The value of this ratio at $t=1$ can be obtained from Eqs. (1) and (6);

$$C_s^{el}/\gamma T_c=(\partial H_c/\partial T)_{t=1}^2(\gamma V_s/4\pi)+1 =-(a_2')^{-1}(\partial h/\partial t)_{t=1}^2+1=2.62. \quad (14)$$

Values calculated from Eqs. (13a) and (13b) differ by as much as 5% in the region of overlap, which establishes the accuracy of the calculations. A major systematic uncertainty is due to the value of $a_2'$ (or $\gamma$). The results of the calculations are shown in Fig. 8, where they are compared with the actual calorimetric data of White, Chou, and Johnston,[25] as corrected for a lattice contribution to the heat capacity, which is shown also. The agreement would seem to be satisfactory in view of the difference in the purity of the samples ($T_c=4.39$°K vs our 4.48°K).

The pressure effect data have been given in Eq. (2) in the form

$$(\partial H_c^2/\partial P)_T=(dH_0^2/dP)\sum_{n=0}^{N} b_{2n}t^{2n}. \quad (15)$$

In this notation, the volume dependence of $\gamma$, which is necessary for the calculation of $\beta_n^{el}$ in Eq. (8), can be expressed as

$$d\ln\gamma/d\ln V=1-(2b_2'/a_2'k)d\ln H_0/dP =1+(2b_2'/a_2')d\ln H_0/d\ln V, \quad (16)$$

where $b_2'$ is used since it is possible that, as in the case of the heat capacity, the power series may not apply to absolute zero. This is not relevant for tantalum. If

$$k=4.5(\pm0.2)\times10^{-7}\ \text{atm}^{-1}$$

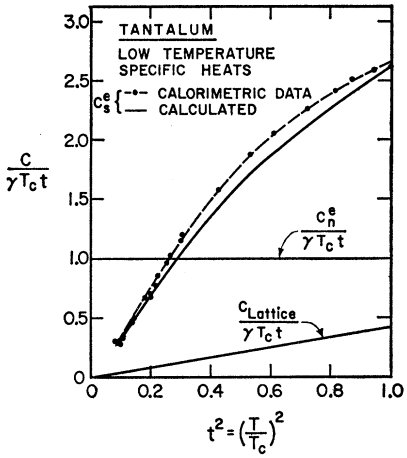


FIG. 8. The calculated electronic contribution to the superconducting heat capacity of tantalum, compared with the direct calorimetric measurements.

is assumed, then

$$d\ln H_0/d\ln V=2.75(\pm0.3)$$

and

$$d\ln\gamma/d\ln V=3.9(\pm0.7),$$

and, from Eq. (8),

$$\beta_n^{el}=1.0(\pm0.1)\times10^{-8}\ T\ \text{deg}^{-1}. \quad (17)$$

$\beta_s^{el}$ can be calculated from Eqs. (8) and (9), and, in terms of Eqs. (10) and (15), becomes, in dimensionless terms,

$$(\beta_s^{el}V/\gamma T_c k)=-a_2't\sum_{n=0}^{N}(nc_{2n}t^{(2n-2)}-c_2'), \quad (18)$$

where $c_{2n}=(a_{2n}+2b_{2n}d\ln H_0/d\ln V)$.

For tantalum, because of the uncertainties in the pressure effect data, this quantity can be written

$$(\beta_s^{el}V/\gamma T_c k)=1.9(\pm0.5)(-0.1t+t^3-0.19t^5) =1.9(\pm0.5)t^3, \quad (19)$$

or,

$$\beta_s^{el}=2.3(\pm0.6)\times10^{-10}\ T^3\ \text{deg}^{-1}.$$

At $T_c$, the ratio of $\beta_n^{el}/\beta_s^{el}$ as calculated directly from Eq. (9) should be approximately 3, in agreement with the above calculation.

## V. CONCLUSIONS

The excellent agreement between directly measured values of $(\partial H_c/\partial P)_T$ and those which can be obtained from critical-field data and $(dT_c/dP)$ measurements (see Fig. 6) removes the discrepancy which was mentioned in the Introduction. Indeed, as purer samples have become available, the $(V_n-V_s)$ data at the transition line appear to be in better agreement with the above results.[7] It would seem that for superconductors thermodynamic quantities which can be measured in zero field may be quite insensitive to impurities, while

those which can be measured only along the transition line require very pure samples. The agreement between the direct calorimetric measurements of heat capacity and the calculated values may be considered as an example. Direct measurements of the thermal expansions also would be of interest. These measurements of the pressure effect are to be preferred to those values which can be deduced from the $\Delta V/V_0$ measurements[7] because of the higher purity of the samples which were used.

Two factors which are involved in the use of the $h^2$ vs $t^2$ representation of experimental critical-field data are worth emphasizing. First, it is possible to use the general shape of the BCS theoretical critical-field curve to establish the limits of error on values of both $H_0$ and $\gamma$ which are obtained by extrapolation. Second, once $H_0$ and $\gamma$ have been determined and the experimental $h^2$ values represented as closely as desired by a power series in $t^2$ over the region of interest, explicit expressions for the heat capacity (and with pressure-effect data, the thermal expansions) can be written down in terms of the appropriate power-series coefficients. This is a convenience for calculation, and is possible only because in practice the rapid $[\exp(-1/t)]$ decrease of the heat capacity as the temperature is lowered occurs only after its influence on the critical-field curve is no longer detectable experimentally.

One application of the combined critical-field and pressure-effect data involves the calculation of the electronic contributions to the thermal expansions of the normal and superconducting states. Tantalum is a poor subject for this type of analysis, since accurate pressure-effect data are difficult to obtain for it.

For many substances, such as mercury, however, the critical-field data as a function of pressure afford perhaps the only means for obtaining these data, since the lattice contribution may be expected to predominate until the thermal expansions are very small. For tantalum, the lattice contribution could be quite small when compared with the electronic contribution, as can be demonstrated by the following argument. If it is assumed to a first approximation that the Mie-Grüneisen equation of state is valid for the metal, the lattice contribution to the entropy can be written as $S(\theta(V)/T)$, and by an argument similar to that which gives Eq. (8),

$$\beta_{\text{lattice}} = -(C_{\text{lattice}} k/V) d\ln\theta/d\ln V = 10^{-10}\, T^3 \text{ deg}^{-1}, \quad (20)$$

where it has been assumed that $\theta$ is the Debye $\theta$ (255°K), and a reasonable value for the Grüneisen constant, $-d\ln\theta/d\ln V = 2$, was used. $\beta_n{}^{\text{el}}$ and $\beta_{\text{lattice}}$ become of the same order of magnitude at 10°K, and at 4°K, $\beta_n{}^{\text{el}}$ is about six times larger than $\beta_{\text{lattice}}$.

Thus, the indications are that tantalum is a very promising substance for which to attempt to detect the existence of the electronic contribution to the thermal expansion by direct measurement.

In principle, it should be possible to determine whether or not the critical curve for tantalum can be expressed in the form $h = f(t)$, where $H_0$ and $T_c$ vary with volume independently. Unfortunately, the precision of the pressure effect data is not great enough to verify this relationship which is implied by the BCS theory.

## ACKNOWLEDGMENTS

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