on the saturating power applied at the frequency $\nu_{13}=\nu_{24}=5.71$ kMc/sec. The general theoretical form of this dependence is contained in Eq. (5) of reference 7 and the form is confirmed by the curves of Fig. 2.[10] The points of the lower curve were determined with the crystal at 4.2°K. Inversion takes place for saturating powers larger than 0.80 mw. For very large saturating powers the experimental curve appears to approach the asymptotic value of Eq. (2), $\chi_{14}''(\infty)/\chi_{14}''(0)=-\nu_{23}/\nu_{14}=-0.186$.

The data of the upper curve of Fig. 2 were taken with the same crystal at the temperature of 1.9°K. Inversion was not observed and the experimental $\chi_{14}''(\infty)/\chi_{14}''(0)\simeq+0.2$. Since the cross relaxation is not temperature dependent we conclude that the condition $T_1^{23}(\mathrm{Cr})/T_1(\mathrm{Fe})\gg1$ is no longer satisfied. We have measured previously[3] this ratio, in a rather preliminary fashion, and found it approximately equal to 85 at 4.2°K and equal to 1 at 1.5°K. The results of the present experiment seem to confirm this very rapid change of $T_1(\mathrm{Fe})$ with temperature.

An experiment was also performed with $K_3Co(CN)_6$ containing 0.5% Cr and 3.0% Fe. Inversion of the ν_{14} line was not observed. Bloembergen *et al.*[7] have discussed the concentration dependence of the cross relaxation in detail. On the basis of their conclusions we interpret our last result as showing the coupling of Fe^{3+} spins not only to the Cr^{3+} spins of ν_{23} transition but also to the spins of other Cr^{3+} transitions.

[10] Exact solution of Eq. (5) of reference 7 for other than simple cases presents an intricate theoretical problem. It has been solved only in certain limiting cases for spin system of one ionic species.

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Some Studies of the Superconducting Transition in Purified Tantalum*

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Extremely sharp magnetic transitions from the superconducting to the normal state are found for highly purified tantalum specimens with residual resistivities approaching $1\times10^{-3}\,\mu$ ohm cm. Negligible flux trapping and pronounced supercooling is found to occur in these samples near the transition temperature T_c.

Values of T_c as high as 4.483°K±.002°K and of the critical field at 0°K, H_0, as low as 830±8 gauss were found for these specimens. The critical field curve is found to have a maximum deviation from a parabolic temperature dependence of about 3%. For tantalum the transition temperature decreases with increasing residual resistivity in much the same way as that observed by Serin and co-workers in dilute substitutional alloys.

Some investigation is made of the current dependence of the resistance transition in a magnetic field.

INTRODUCTION

TANTALUM metal has in the past presented great problems in purification which limited measurements of the superconducting properties to impure specimens. Numerous authors[1] have investigated various properties of tantalum and in many instances have obtained significantly different results. Quoted values of H_0, the critical field at absolute zero vary by several hundred gauss while quoted values of T_c differ by as much as 0.2°K.

In most measurements broad transitions, spurious hysteresis effects, and pronounced flux trapping were observed. These effects are seen to be largely attributable to the presence of small amounts of interstitial impurities, viz., hydrogen, carbon, oxygen, nitrogen, in the tantalum lattice.[2] Recently several authors[3–5] have shown that purified tantalum yields quite different values of H_0 and T_c.

Preliminary experiments in our laboratory indicated that specimens could be prepared with much lower

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[1] W. Meissner, Z. Physik **61**, 191 (1930); K. Mendelssohn and J. R. Moore, Phil. Mag. **21**, 532 (1936); J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937); F. B. Silsbee, R. B. Scott, and F. G. Brickwedde, J. Research Natl. Bur. Standards **18**, 295 (1937); J. G. Daunt, A. Horseman, and K. Mendelssohn, Phil. Mag. **27**, 754 (1939); W. H. Keesom amd M. Desirant, Physica **8**, 273 (1941); W. T. Zeigler, W. F. Brucksch, Jr., and J. W. Hickman, Phys. Rev. **62**, 354 (1942); H. Preston-Thomas, Phys. Rev. **88**, 325 (1952); R. T. Webber, Phys. Rev. **72**, 1241 (1947); R. D. Worley, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **91**, 1567 (1953); K. Mendelssohn, Nature **148**, 316 (1941).

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

[3] C. Chou, D. White, and H. L. Johnston, Phys. Rev. **109**, 797 (1958).

[4] K. Mendelssohn, *Proceedings of the International Conference on Electron Transport in Metals and Solids* [Can. J. Phys. **34**, 1315 (1956)].

[5] A. B. Calverley (private communication).

residual resistivity values than previously reported. Subsequently a detailed study[6] of the purification of tantalum led to a method for preparing small size specimens with residual resitivities approaching $10^{-3}\,\mu$ ohm cm, i.e., in the range expected for zone refined material.

It was therefore felt that a systematic study of the resistive and magnetic properties of the superconducting transition of such material would be of value since one could observe properties more nearly characteristic of the metal.

Recent measurements of Swenson[7] on the pressure dependence of the critical field and by Olsen and Rohrer[8] of the length change at the superconducting transition of specimens of IBM purified tantalum show extremely sharp and reproducible transitions.

EXPERIMENTAL DETAILS

Sample Preparation

All measurements were made on wires varying in diameter from 10 to 40 mils. Tantalum obtained from the National Research Corporation was always found to have an extremely low residual resistivity after our purification treatment.

The wires were placed in a high vacuum system containing an oil diffusion pump. The system was baked for several hours before the degassing of the wires was begun. The degassing procedure which progressed through several stages of development essentially amounted to heating the wire to a temperature between 2400°C and 2800°C by passing alternating current through it while in a vacuum which ultimately reached a value between 2×10^{-7} and 2×10^{-10} mm Hg. The specimen was heated for times up to several hours. In some cases the wire was cycled in temperature to avoid heating the walls of the vacuum system, while in other cases continuous heating was made possible by the use of a liquid nitrogen cooled vacuum jacket. By varying the time, temperature and pressure of this process, wires with large ranges of Γ were produced. $1/\Gamma$ will denote the resistance ratio $R_0/(R295°\mathrm{K}-R_0)$, where R is the resistance, and R_0 the residual resistance. The quantity $1/\Gamma$ is a measure of purity and is proportional to the total scattering cross section for the electrons, independent of the specific impurity responsible.

This technique which is fully described elsewhere[6] will remove quite rapidly the fairly mobile gaseous impurities and for long treatment times has been shown to be effective in removing certain substitutional impurities (probably iron, niobium and silicon).

For larger size specimens it was not possible to obtain purity comparable with that achieved for the 10-mil wire diameter. This is partially due to the longer cool-down time for these samples which permits more back diffusion of gases into the specimen while it cools, thus possibly producing a decrease in purity as well as a decrease in homogeneity.

A special effort was made to remove the carbon impurity and at the same time to lessen the effect of back-streaming from the diffusion pump. After a brief degas near 2800°C, oxygen at pressures varying from 10^{-6} to 5×10^{-4} mm Hg was continuously bled into the system with the wire held near 2200°C. After this oxygen treatment, which lasted from 15 to 20 minutes, the wire was degassed at 2800°C at the ultimate system pressure for times varying up to 75 minutes. This procedure produces specimens having the highest Γ or, what is equivalent, the longest electronic mean free path. Reference to the literature revealed that this procedure[9] successfully removes carbon from tungsten.

Our most extensive work was done on polycrystalline wires with sizes varying from 10 to 40 mils and only in several instances were single crystal specimens used. The measurements covered Γ values ranging from about 10^4 to 10.

Apparatus and Procedure

A conventional all glass cryostat was used for the measurements. The pressure above the bath was stabilized by means of a bellows type manostat. In order to obtain temperatures above 4.2°K the bath was held under an overpressure while being violently mixed by an electrical heater until equilibrium was reached. The bath was electrically stirred during all measurements and corrections for the hydrostatic head were made in a conventional manner. After our measurements were almost complete, some results of other investigators[10] indicated that this type of correction may not always yield the true bath temperatures. However, our resistance sample holder always contained 4 specimens so that relative values of H_c and T_c could be obtained with high precision. The values of H_c and T_c for the standard sample were always found to be reproducible within our limits of accuracy.

The vapor pressure was monitored by a differential oil manometer and read from a precision U-tube manometer with the reference side maintained under a vacuum. A Wild cathetometer was used to read the mercury level to a precision of 0.02. mm. The T_{55E} scale was used to determine the temperatures.

A six dial Rubicon microvolt potentiometer was used to measure the residual resistance ratios.

For the resistance transition measurements, fine wire pressure contacts were used initially for the less pure samples while silver painted voltage contacts were used for the final measurements on the very pure material to minimize the effects of strain. The sample holder always contained at least four samples, one of which remained

[6] D. P. Seraphim, J. I. Budnick, and W. B. Ittner, III, Trans. Am. Inst. Mining, Met. Petrol. Engrs. (to be published).
[7] C. A. Swenson (private communication).
[8] J. L. Olsen (private communication).
[9] R. E. Schlier, J. Appl. Phys. **29**, 1162 (1958).
[10] F. E. Hoare and J. E. Zimmerman, Rev. Sci. Instr. **39**, 184 (1959).

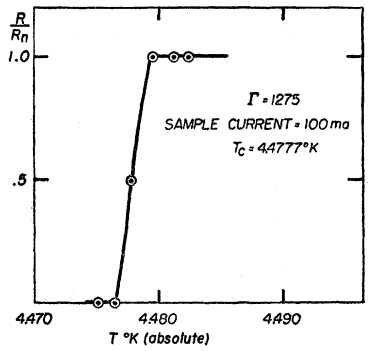

FIG. 1. Resistance versus temperature in the earth's field for 10-mil tantalum wire.

as a comparison standard from run to run. It was found[11] that a light spotweld of silver painted voltage connections while in the helium bath greatly reduced noise, and at the same time did not produce any broadening of the transition. Connections which were spotwelded in air always produced a marked broadening in the transitions and such samples were not used in any reported measurements.

A Librascope X-Y recorder driven by a Liston Becker chopper amplifier was used to plot the resistance field transitions. A well regulated supply furnished the current. A buckout circuit was used on the field axis so that the width and shape of the transitions could be studied in great detail. Data obtained from the plotter measurements agreed with those taken potentiometrically. Both a water cooled and a liquid nitrogen cooled Garret[12] type solenoid were used to provide the total magnetic field at the lowest temperatures. The field was always uniform over the measured part of the sample to better than 0.3% and at high temperatures when one coil was used approached a uniformity of 0.1%. Nuclear magnetic resonance was used to calibrate the coils to an accuracy of about 0.05% while current readings could be made to better than 0.1%. A Helmholtz coil was used to buck out the horizontal component of the earth's field while compensation for the vertical component was made in the measurements.

The sample holder used in the magnetization measurements was of the type used by Shoenberg.[13] In a field less than H_c the sample was dropped from one coil to another and the resulting deflection on a ballistic galvanometer was observed as a function of the applied field. In these measurements a small positive pressure jump occurred on dropping the sample. By waiting for about $\frac{1}{2}$ min between successive measurements, the effect of this small temperature change on the magnetization measurement could be neglected. In our setup it was not possible to measure simultaneously the flux and resistance transitions of these small specimens.

[11] R. A. Connell (private communication).
[12] M. W. Garrett, Jr., J. Appl. Phys. 22, 1091 (1951).
[13] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), p. 53.

EXPERIMENTAL RESULTS

Resistance Transitions

A plot of the resistance versus temperature taken in the earth's field is given in Fig. 1. In the pure samples, i.e., those with a Γ greater than several hundred, the transitions are of the order of 1–3 millidegrees in width and behave properly with changes in measuring current. No detailed measurements were made of the functional relationship of T_c on the measuring current used. The values of T_c obtained from the directly measured resistance transition agreed within 1 to 2 millidegrees with those obtained from extrapolation of the magnetic field data. In Figs. 2 and 3 tracings of some representative plotter data are shown for the resistance as a function of applied field taken at constant temperature. From these plots the critical field for the resistance transition was obtained. There are several things to be noticed in these measurements. In the purest samples from about $t=0.8T_c$ up to T_c, the resistance is extremely sharp as seen in Fig. 2, the best samples being about 0.3% H_c in width. The measuring current density, when small, has no effect on the shape of the transition, thus allowing an unambiguous determination of H_c.

As the temperature is lowered the resistance transition begins to broaden as shown in Fig. 3. These curves are all taken at the same temperature with the measuring current increasing from 1 to 10 milliamperes and show a marked current dependence in the initial part of the transition. An abrupt spike beginning the transition could be clearly seen as the measuring current was increased. The spike whose height is strongly dependent on the measuring current is only slightly affected in position by the relatively small changes in magnetic field produced by the measuring current changes. It is always followed by a very broad region until the full normal resistance is restored. Ballistic measurements show this spike to occur at the critical field for flux penetration while a field much greater than this was required to restore the full normal resistance. The

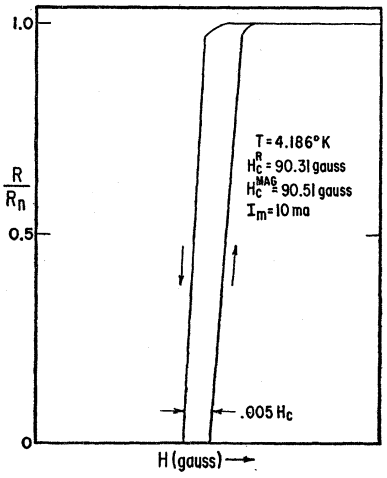

FIG. 2. Resistance versus magnetic field near T_c.

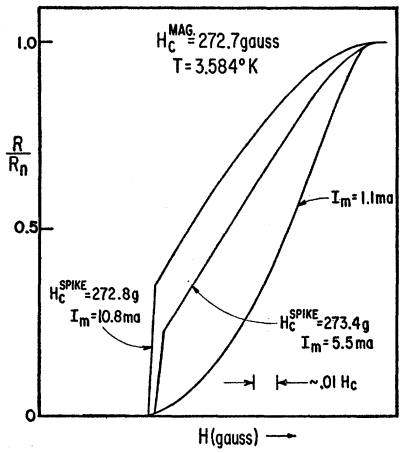

FIG. 3. Resistance versus magnetic field at a lower temperature for the same sample with measuring current values of 1.1, 5.5, and 10.8 ma.

characteristics of this type of behavior has been investigated more fully by Seraphim and Connell.[14]

In the limit of small measuring currents very broad transitions occur at the lowest temperatures. Increasing the measuring current produces this small spike-like return of resistance demonstrating the separation into the bulk and filament transitions region reported by Preston-Thomas.[1]

This broadening of the resistance seems to occur in a fairly definite temperature range for any given sample. In general, the better the sample the lower a temperature is needed before broadening sets in. A plot illustrating separation between the bulk H_c (the H_c gotten from the initial rise in R_n) and the H_c needed to restore $\frac{1}{2}R_n$ (at small measuring currents) is shown in Fig. 4. These measurements were all made at constant measuring current.

Similar types of transitions have been observed by Doidge[15] and Reeber[16] in studies of substitutional solid solutions of tin and indium.

Doidge suggests an explanation for his results on well annealed monocrystals in terms of a theory proposed by Pippard[17] which relates the interphase surface energy to the normal electronic mean free path. As the mean free path is decreased by scattering the surface energy is lowered. Thus as one goes to shorter and shorter normal mean free paths there may appear regions of negative interphase surface energy which permit a zero resistance current path even though the flux penetration is essentially complete. Therefore a field higher than the bulk critical field for flux penetration is required to restore the resistance in this region. Clearly, local strains or inhomogeneities may, in general, provide such regions in which the interphase surface energy is decreased below that for the ideal material. Our preparation techniques do not rule out such possibilities since our samples, which are polycrystalline, do not cool uniformly after degassing. This probably results in a small gradient of impurity along the length of the sample as well as possible gradients near the grain boundaries. Thus, at temperatures below T_c the surface energy can become negative in small regions, thereby broadening the resistance transition, since these regions would remain superconducting in fields greater than the bulk critical field. To quantitatively account for the detail of the shape of the resistance transitions a very complicated network of regions spread along the sample would be required. No attempt has been made to analyze this situation in detail.

At temperatures close to T_c in samples of high Γ a marked resistance hysteresis is observed as shown in Fig. 2. This hysteresis, characterized by a discontinuous normal to superconducting transition, has been shown to be supercooling by magnetization measurements. As the temperature is lowered the hysteresis diminishes in size. No detailed study of the behavior of the hysteresis will be presented in this paper. In general, in studies of rather impure samples other types of hysteresis along with an increase in dH_c/dT near T_c are found. It will be shown that the transition temperature is always depressed in going to less pure samples.

In our earliest measurements an observation was made of the effect of very slowly cooling a specimen from its high purification temperature. Under these circumstances there seems to be a difference between a single and polycrystal specimen. A single and a poly-

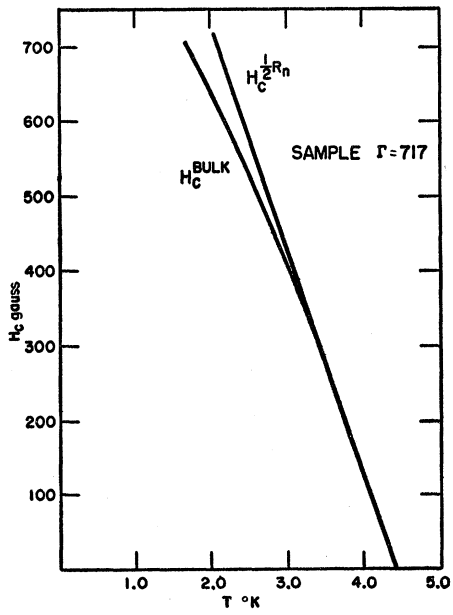

FIG. 4. Critical field versus temperature showing the separation between the bulk critical field and the field necessary to restore $\frac{1}{2}R_n$.

[14] R. A. Connell and D. P. Seraphim, Phys. Rev. **116**, 606 (1959).
[15] P. R. Doidge, Trans. Phil. Soc. (London) **A248**, 553 (1956).
[16] M. Reeber, Phys. Rev. **117**, 1476 (1960).
[17] A. B. Pippard, Proc. Dambridge Phil. Soc. **47**, 617 (1951).

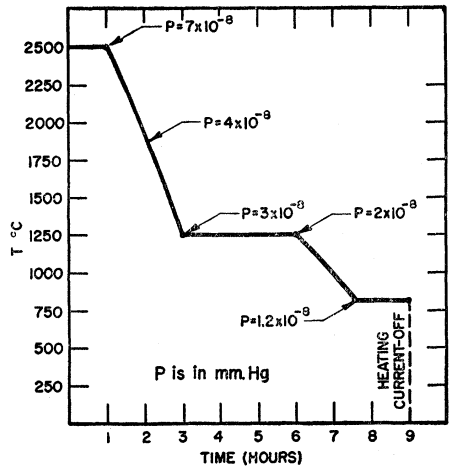

FIG. 5. Illustration of cooldown procedure for 2 degassed samples, one a single crystal, the other a polycrystal.

crystal wire were simultaneously degassed at high temperatures and subjected to all treatments as equally as possible. After degas the wires were subjected to the treatment shown in Fig. 5. This amounts to a slow cooldown over two regions and to an aging process at two elevated temperatures. Although the samples had approximately the same values of Γ (i.e., 129 and 140, which are rather low) they exhibited quite different resistive transitions as shown in Fig. 6. They were by no means very good specimens. In the single crystal the slope of the critical field curve near T_c is less than $\frac{1}{3}$ that of the polycrystal. At this low measuring current the resistive transition for the single crystal was at least an order of magnitude sharper than that of the polycrystal.

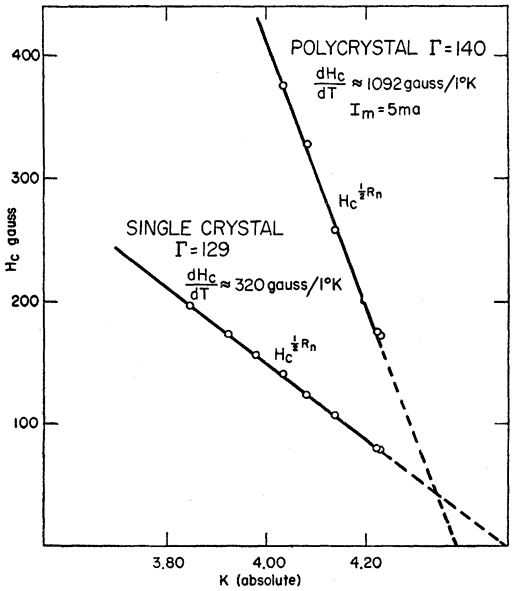

FIG. 6. Illustration of difference in critical field slope between treated single and polycrystal samples.

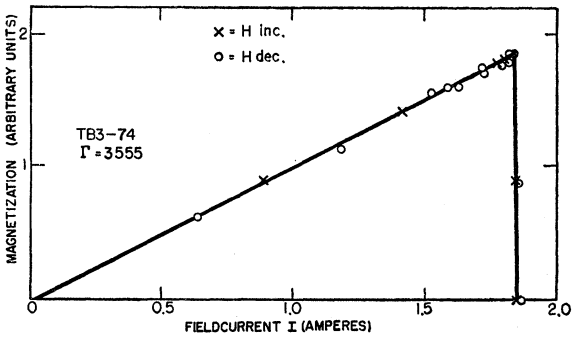

FIG. 7. Magnetization curve for medium purity 10-mil tantalum wire.

The dotted lines are put in to show the effect of a long extrapolation in finding a value for T_c. This method of extrapolation of resistive critical field curves was never used in obtaining the T_c values later reported. The type of behavior shown in Fig. 6, viz., the high $(dH_c/dT)_{T \to T_c}$ is a characteristic of formerly so called "hard" superconductors and is here probably the result of both filamentary networks of gaseous impurities along the grain boundaries[18] as well as smaller inhomogeneities within the grains. On slow cooling, we feel that, in general, there is always some ordinary bulk gas diffusion into the degassed specimens, and in addition, in the polycrystal specimen some rapid diffusion along the grain boundaries even at relatively low temperatures. The probable resulting strain and inhomogeneity from this selective clustering of gaseous impurities at the grain boundaries and near the surface can have a pronounced effect on the resistive transition. To date no extensive study of this effect in both polycrystal and single crystal specimens has been carried out. All of the measurements which we will report were done on poly-

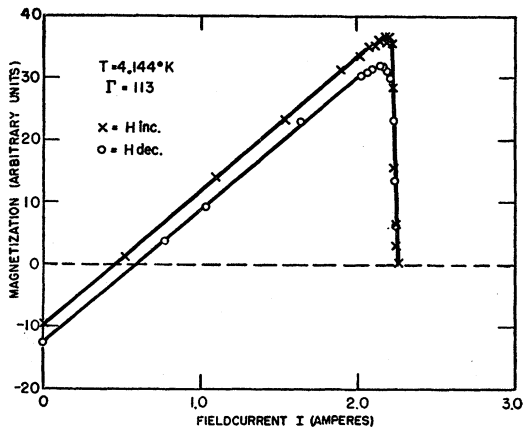

FIG. 8. Magnetization curve for low purity 40-mil wire.

[18] E.g., see C. Zwikker, *Physical Properties of Solid Materials* (Interscience Publishers, Inc., New York, 1954), p. 187 ff. also Donald P. Smith, *Hydrogen in Metals* (University of Chicago Press, Chicago, Illinois, 1947); and G. L. Miller, *Tantalum and Niobium* (Academic Press, New York, 1959), Chap. 10.

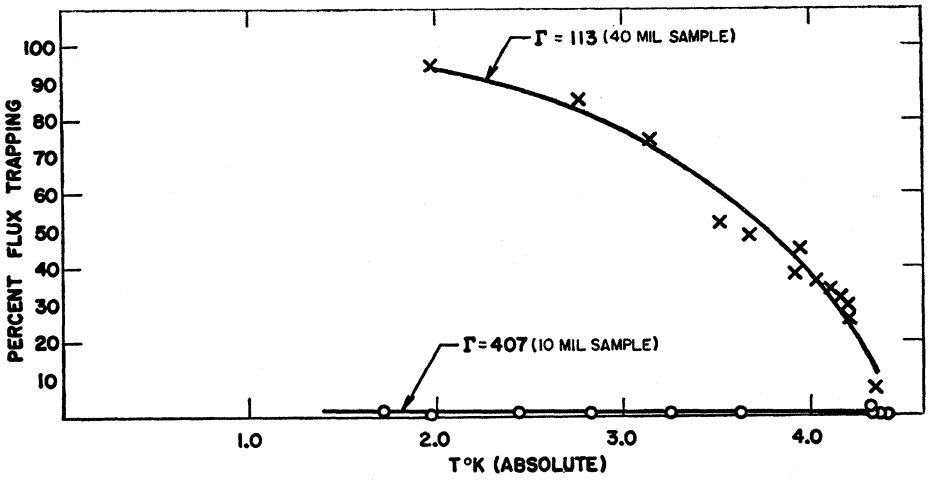

FIG. 9. Flux trapping for both low and high purity samples.

crystals which were cooled rapidly enough to show no sign of such broadening. These all had the same low value of $(dH_c/dT)_{T \to T_c}$ and could therefore be regarded as well behaved superconductors.

Magnetization Measurements

The magnetization measurements were made on small diameter wires oriented parallel to the applied field and long enough so that demagnetization effects could be neglected.

In Fig. 7 is plotted the magnetization versus applied field and it is apparent that for a sample whose resistance ratio is several thousand the transition is extremely sharp. For less perfect samples the magnetization curves are almost as sharp but there is an appreciable amount of flux trapping as shown by Fig. 8. In Fig. 8 the initial zero field intercept denoted by the × line corresponds to the remanent moment at the previously measured temperature while the lower intercept gives the value of the remanent moment at the measuring temperature and is obtained when the field is removed. In such samples this remanent moment increases very rapidly with temperature. Figure 9 shows the marked difference in flux trapping between two samples of different resistance ratios. The measure of flux trapping used is the ratio of the remanent paramagnetic moment in zero field to the maximum diamagnetic moment which occurs at H_c. Here, the Γ values are only convenient labels for samples and we do not present a systematic relation between Γ and the amount of flux trapping observed. The apparatus we used did not permit the flux trapping to be measured to better than 2 or 3%.

Electrolytic polishing and etching of tantalum, which is known to introduce interstitial hydrogen quite readily,[19] produces marked effects on the magnetization curves. The transition is broadened and the sample is left with a large remanent moment after etching. Apparently enormous surface strains[19] produced by the electrolytically absorbed hydrogen, which initially at least, is concentrated near the surface, succeed in producing large flux trapping. That this behavior results from effects produced in the surface layer of the sample is borne out by several simple surface treatments. In Fig. 7 is shown the magnetization curve for a high purity sample which has been lightly sandblasted. Figure 10, curve A, shows the same sample after the ends have been lightly etched. Here there is a broad transition and the appearance of some supercooling hysteresis. A light sandblasting of the surface of this sample will restore the sharp transition, as shown in Fig. 7, but with some added hysteresis of a value comparable to that shown in curve A. Electrolytic polishing of the sample for several minutes yields the magnetization curve B shown in Fig. 10. The value of the moment is greatly reduced, the transition is smeared out, and the sample now traps substantial flux. In curve B the ordinate is the measured moment of the sample divided by the moment before polishing. Surface sandblasting of this sample after the

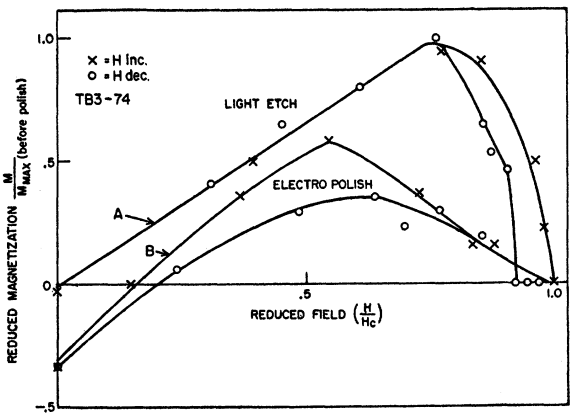

FIG. 10. Curve A (reduced magnetization versus field for lightly etched wire;. Curve B (reduced magnetization versus reduced field for electrolytically polished wire).

[19] Donald P. Smith, reference 18, Sec. 10.8.

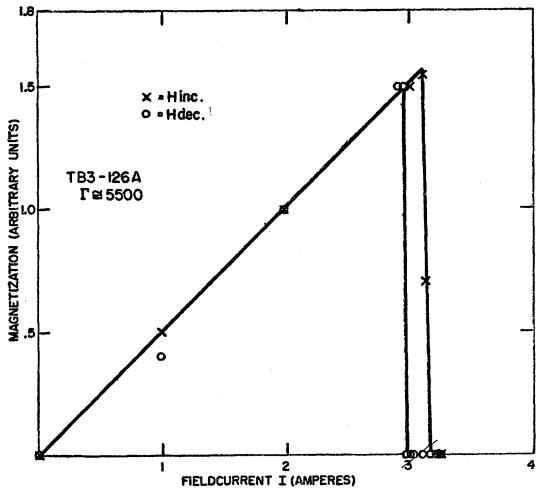

FIG. 11. Magnetization curve for high purity sample which exhibits supercooling.

polish showed the magnetization curve to be much improved and to approach its original shape. In waiting some time at room temperature between measurements we also probably allow the very inhomogeneous hydrogen concentration at the surface to become somewhat more homogeneous. This also tends to improve the transition. No systematic measurements were made to check the dependence of the magnetization curve upon the time the sample was left standing at room temperature. We tentatively assert that the large effects of polishing shown in Fig. 10 are the result of hydrogen,[19] liberated in the region of the surface, and that the hydrogen remains inhomogeneously distributed in the sample for some period of time.

Figure 11 shows a magnetization curve for an extremely pure sample which shows a discontinuous transition from a supercooled state to the stable superconducting state. The degree of supercooling is quite marked in very pure samples and it should be possible in this material to measure the ideal supercooling near T_c which was studied by Faber[20] for tin and indium. Such studies could be used to provide some measure of the surface energy parameter Δ for pure tantalum. This direct observation of supercooling is strong evidence for the high perfection of the purified material and has never been reported before in tantalum. That supercooling is responsible for the hysteresis in the resistance transition was also verified in reference 14.

Critical field curves and the dependence of T_c on Γ. As pointed out above, for temperature near T_c, both the resistance and flux transitions are coincident but at lower temperatures the full normal state resistance is restored only at fields much greater than the true thermodynamic critical field.

In Fig. 12 the thermodynamically significant critical field curve obtained from magnetization measurements is shown for a typical high Γ sample. H_0 can be determined graphically by extrapolating on a t^2 plot where t is the reduced temperature. There is a small deviation from a parabolic curve drawn for the appropriate H_0 and T_c.

Little difference is found in the shape of the critical field curve for samples with Γ values greater than several hundred.

A polynomial, without a linear term in temperature, has been fitted to our data using an IBM-704 computer. From this we can determine H_0 and T_c[21–23] and also an appropriate value for γ, the coefficient of the normal state electronic specific heat. The highest power used in our curve fitting was cubic and the expressions for the reduced critical field $h \equiv H_c/H_0$ for several samples are given in Table I along with the corresponding values of γ, H_0, T_c, and $(dH_c/dT)_{T \to T_c}$. The latter is some measure of the so-called softness of a superconductor and in this sense all the purified samples are well behaved, in that they have roughly the same low slope near T_c.

It should be noted that for sample TB2-126A, a_2, a_3, and H_0 are all higher than the values given for the other 3 samples. At low temperatures for this sample a hysteresis of about 0.5% in the magnetization curve was found, thus complicating the determination of H_c. The type of hysteresis we observe in this sample seems to be similar to that observed and discussed by Decker.[21]

TABLE I. Summary of critical field data for several tantalum samples having different Γ values.[a]

Sample No.	$1/\Gamma \times 10^4$	a_2[b]	a_3	$\gamma \times 10^{-4}$ ergs/mole deg^2	H_0 (Gauss)	T_c°K	$(dH_c/dT)_{T \to T_c}$ gauss/°K
TB18A	95.2	−1.196	+0.222	7.03	821	4.457	−320
TB2-28A	14.1	−1.218	+0.217	7.26	830	4.477	−323
TB2-29A	26.4	−1.214	+0.215	7.29	833	4.475	−325
TB2-126A	1.82	−1.266	+0.265	7.83	846	4.482	−317

[a] The estimated uncertainty in the value of H_0 here given should be less than 1%. The value listed in the table is the one calculated which agrees to much better than ½% with that obtained by extraploation. The uncertainty in T_c is about 2 millidegrees while that in dH_c/dT is about 2%.
[b] $h = 1 + a_2 t^2 + a_3 t^3$.

[20] T. E. Faber, Proc. Roy. Soc. (London) **A241**, 531 (1957).
[21] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).
[22] R. D. Worley, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **99**, 447 (1955).
[23] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).

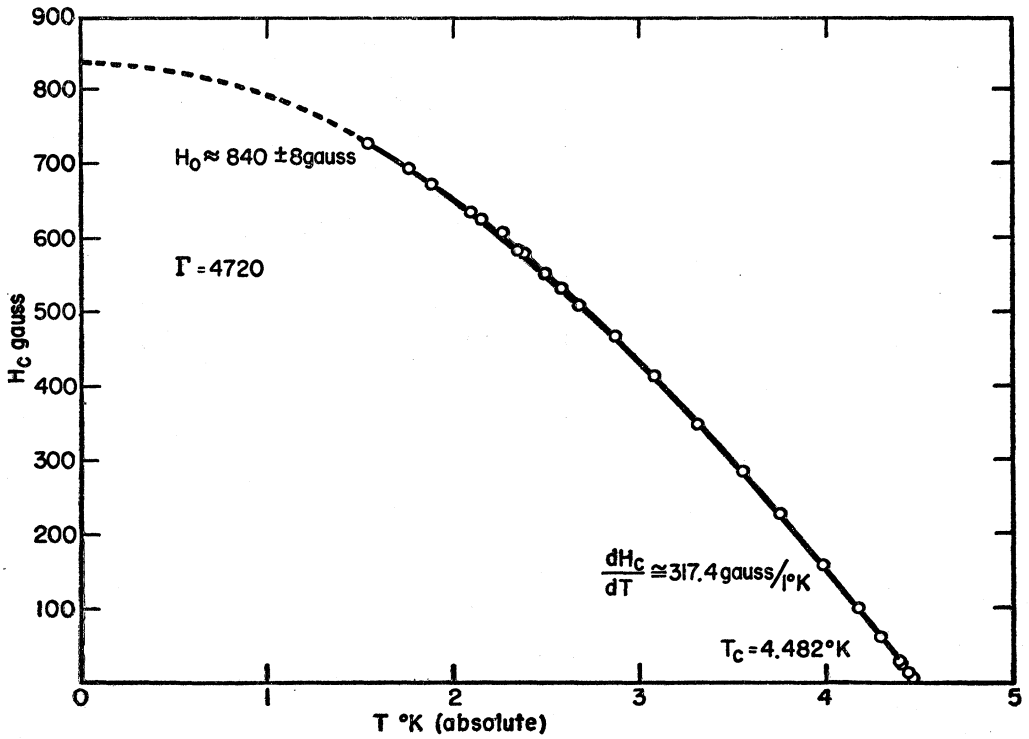

FIG. 12. Critical field versus temperature for high purity sample.

The other samples listed showed no behavior of this type down to the lowest temperature measured and should better represent the actual threshold field data for tantalum.

The temperature variation of our data for H_c is plotted in Fig. 13 along with data for the critical field of tin and a theoretical curve from the BCS theory. The deviation from parabolic is quite close to that of tin, which has about the same ratio of T_c to Θ, where Θ is the Debye temperature. Its maximum deviation from the parabolic curve thus agrees with the empirical relation pointed out by Mapother in which this maximum deviation varies linearly with the ratio of T_c/Θ. The values of γ we obtain are in poor agreement with those given in references 3 and 22, viz., 5.7 and 5.4×10^4 ergs/mole deg^2, respectively. We expect values which are too high and not in very good agreement with the calorimetric value for reasons outlined by Lynton *et al.*[23] and Mapother.[24]

The transition temperature has been measured for samples with Γ values varying from about 8000 to 10. In purifying the specimens both interstitial and substitutional impurities are removed, and no determination is made of the absolute amount of any one species which is present. Quite independently of the nature of the impurity present the value of Γ should be proportional to the normal state mean free path. T_c values have been obtained both by direct resistance measurements and by extrapolation of the critical field curves for both resistive and magnetic transitions. Whenever two or more means of determining T_c were used, the values of T_c obtained agreed within our experimental error.

A corollation between Γ and T_c was first pointed out by Serin, Lynton and co-workers.[23] In their experiments T_c was always found to be initially depressed as one added substitutional impurities. This initial decrease in the transition temperature was found to be independent of the impurity and to be proportional to the change in mean free path as deduced from measurements of Γ.

Figure 14 shows the same general behavior for tantalum recalling that in these measurements both interstitial and substitutional impurities are involved. The

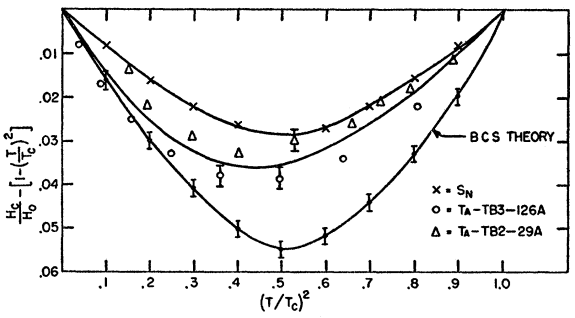

FIG. 13. Deviation from parabolic threshold field curve for Ta, Sn, and BCS theory. Estimates of uncertainty are included for only a few Ta points.

[24] D. E. Mapother (private communication).

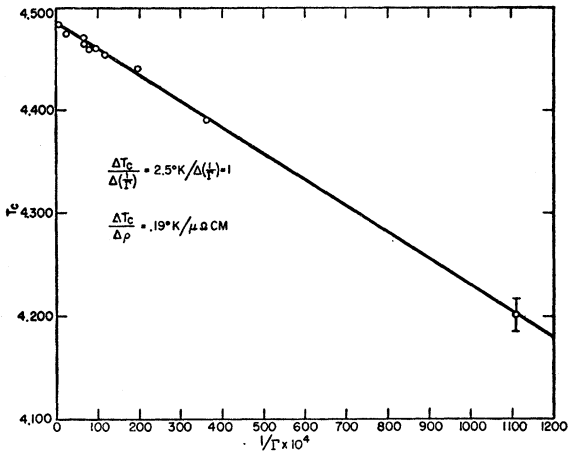

FIG. 14. Variation of T_c with normal state electronic mean free path.

slope of ΔT_c versus $1/\Gamma$ is quite comparable to that obtained by Serin and co-workers for tin. From these measurements we conclude that in tantalum T_c is most strongly dependent on the electronic mean free path and varies in an approximately linear fashion with $1/\Gamma$.

CONCLUDING SUMMARY AND DISCUSSION

By degassing tantalum in high vacua at temperatures close to the melting point, large amounts of interstitial along with some substitional impurities can be removed. Samples prepared in this manner exhibit good superconducting behavior with sharp magnetization curves and little or no flux trapping. Reliable and meaningful interpretation may thus be applied to measurements on such materials.

The measured tantalum wires were found to exhibit sharp resistance transitions near T_c which at lower temperatures may be more clearly characterized by an initial spike-like appearance of resistance followed by a broad restoration of the total resistance. The height of the spike-like region is extremely sensitive to the measuring current while its position remains at that of the critical field for flux penetration. We attribute this type of behavior to small inhomogeneities or filamentary regions of impurities which cause locally negative values of interphase surface energy to exist in the sample even after purification. The cool down rate of the samples from the degas temperature does not preclude such possibilities. No detailed microscopic interpretation of these observations is presently possible from this work.

This resistance transition behavior is to be compared to the observed magnetization curves which are very sharp and not especially sensitive to small amounts of impurity, which is what one would expect, since in the magnetic measurements a volume property is being observed.

The observation of pronounced supercooling near T_c after special treatment of the samples is good evidence of the high degree of purity attained and may permit meaningful values of the interphase surface energy to be determined. Surface inclusion of hydrogen is thought to be responsible for drastic effects on the magnetization curves of high purity tantalum.

A reliable value of H_0 and T_c has been determined for "pure" tantalum from the critical field data. $H_0=830 \pm 8$ gauss, $T_c=4.482\pm.002°K$. Only an approximate value of γ can be calculated from our data.

Initially, the transition temperature of tantalum is found to decrease linearly with increasing residual resistivity. This is another example of a general type of mean free path behavior first pointed out by Serin, Lynton and co-workers in dilute substitional alloys.

It is felt that similar treatment of the other so-called "hard" superconductors should result in equally good superconducting properties.

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