Superconducting Properties of Technetium*

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Isothermal magnetization measurements are reported for technetium in the superconducting state from 1.5°K to the transition temperature after various stages of heat treatment up to 2000°C. The purer sample studied ($\Gamma=120$, where Γ is the ratio of resistance at 295°K to the resistance at 9°K) was found to have a transition temperature of 7.73 ± 0.02°K, and was destroyed in an early attempt at annealing, while the second sample ($\Gamma=97$), which had a transition temperature of 7.77 ± 0.02°K, was studied more thoroughly. The magnetic behavior of this material is characteristic of a type-II superconductor, and the experimental temperature dependence of H_{c2}, the upper critical field, is compared with existing theories. Upper limits to the thermodynamic critical field $H_c(t)$, which have been obtained by integrating under the nonreversible magnetization curves observed after the 2000°C heat treatment, lead to an extrapolated value of $H_c(0)=1410$ Oe, and a Ginzburg-Landau parameter of $\kappa_1(1)=0.92$. The data suggest that technetium is a weak-coupling superconductor of the BCS type, and the results are examined for self-consistency.

I. INTRODUCTION

IT is only recently that gram quantities of technetium metal have become available from nuclear-fuel reprocessing, so that, understandably, earlier investigations of the superconducting behavior of technetium have been limited to transition-temperature determinations.[1–3] A detailed study of this element, then, seems warranted, since the experimental data might contribute toward a better understanding of the basic mechanisms of superconductivity, as well as serve as a base for the preparation of interesting type-II superconducting alloys. Bulk magnetic properties of technetium in the superconducting state have been reported by Trojnar *et al.*[4] Examination of their results and cited spectrographic impurity analysis indicates that their sample was somewhat less pure than those investigated in this work. We have examined the bulk magnetization of superconducting technetium from the transition temperature down to 1.5°K for varying degrees of sample perfection. Allied experiments such as resistive transition measurements were carried out, and the results are discussed in terms of the present-day theory of type-II superconductors.

II. SAMPLE PREPARATION AND ANNEALING TREATMENT

Tc^{99} (the isotope available for study) has a radioactive half-life of approximately 2×10^5 years, the activity being primarily due to the emission of 0.29-MeV β particles. This activity can be easily shielded by a plastic coating or metal foil, but glove-box procedures are required to prevent direct-contact contamination during sample manipulation. The samples consisted of rods 25 mm in length and 3 mm in diameter, with the edges of the rod rounded to approximate ellipsoidal geometry. During the course of the investigation, "as-received" samples were furnished by one of us (G.R.L.), and since a detailed account of the sample preparation is published elsewhere,[5] only the analysis of the as-swaged ingot is reproduced here as Table I. The impurity concentrations given establish a lower limit on the purity of the sample, inasmuch as the hot-cell analytic techniques can introduce traces of copper and aluminum.

The "as-received" materials are severely cold worked, leading to superconducting-to-normal resistive transitions occurring over a wide temperature interval,[6] as well as highly irreversible magnetization curves. For this reason, annealing of the polycrystalline samples was carried out at progressively higher temperatures, with magnetization measurements undertaken after each heat treatment, and with occasional auxiliary resistive measurements. For annealing in reducing atmospheres at temperatures up to 1200°C, a nichrome

TABLE I. Analysis of as-swaged technetium ingot.

Element[a]	Amount (ppm)
Fe	10 ± 10[b]
Cu[c]	50 ± 50
Al[c]	330 ± 50
O_2	15 ± 15[d]

[a] Elements also sought but not detected included Cr, Ni, Co, Na, Si, Ti, V, and Zr.
[b] In each case, the confidence limits also represent the threshold values for detection of the element.
[c] It is possible that hot-cell analytic techniques may introduce traces of Cu or Al.
[d] Oxygen analysis obtained by neutron activation.

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resistance furnace with a mullite muffle tube was used. Samples for heat treatment were placed in an alumina boat in the mullite tube, and the reducing atmosphere consisted of commercially pure H_2 at a pressure of 1 atm. Some heat treatments at temperatures between 1000 and 1500°C were made in a Ta element resistance furnace, in a vacuum corresponding to a pressure of less than 1×10^{-6} mm Hg. Heat treatment in either a vacuum or in hydrogen at a given temperature resulted in similar changes in the superconducting behavior, as well as similar changes in the residual resistivity, indicating that no undesirable chemical changes occurred using the reducing atmosphere.

For annealing treatments above 1500°C, we are indebted to James M. Leitnaker of the Metals and Ceramics Division at Oak Ridge National Laboratory. The apparatus he employs consists of a 20-kW vacuum-induction furnace with an eddy-current concentrator, and has been described previously.[7] While temperatures in excess of the melting point of Tc (2140°C) are attainable, the maximum annealing temperature in this work was 2000°C. The samples were supported in a tungsten crucible which also served as the rf susceptor, and, following the initial out-gassing, the pressure in the system was 1×10^{-6} mm Hg for annealing times of 1 h. In order to minimize direct contact of the sample with the tungsten walls, the interior of the crucible was first coated with technetium by heating a small amount of the metal in the crucible at 2000°C prior to any annealing treatments. There was no evidence of the sample welding to the crucible, and the experimental data given in Sec. IV indicate that diffusion of tungsten into the sample was negligible.

III. LOW-TEMPERATURE MEASUREMENTS

Isothermal magnetization measurements were of the ballistic type, and consisted of moving the sample in a uniform longitudinal magnetic field from one flux-sensing coil to another connected in opposition, and measuring the resultant pulse on a ballistic galvanometer. The uniform magnetic field was supplied by a sixth-order superconducting solenoid capable of generating a maximum field of 15 kOe. The effective sensitivity of ballistic galvanometer, sample mass, and sensing coils corresponds to a flux density of 0.2 G. Starting with the sample in zero field and with zero sample remanent magnetic moment, measurements were made in monotonically increasing fields, until the upper critical field H_{c2} was exceeded. Similar measurements were then made in decreasing fields. The demagnetization factor of the samples was taken into account by studying samples of Pb and annealed Nb of identical geometry.

For the temperature region above 4.2°K, the sensing coils and the sample, which was mounted on a rod, could be isolated from the helium bath in a tube containing helium exchange gas at a pressure of about 5 mm Hg. Power was supplied to a Pt-Rh heater wound bifilarly and nonuniformly about the apparatus to establish a uniform temperature zone in the sensing coils. A Minneapolis-Honeywell Ge-thermometer was employed for temperature determinations to an estimated accuracy of ±0.02°K. Below 4.2°K the apparatus was immersed in the helium bath at controlled pressures. Helium vapor-pressure measurements were used for thermometry, with the Ge thermometer serving to indicate the establishment of thermal equilibrium.

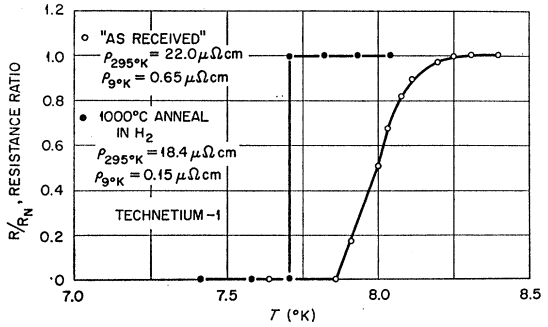

FIG. 1. Resistive transition of technetium versus temperature. Open circle—"as-received"; closed circle—heat-treated at 1000°C for 8 h.

To study the superconducting-to-normal resistive transitions and to measure the normal-state residual resistivity, the sample and a Ge thermometer were mounted in a copper can, which was isolated from the He bath. The temperature of the assembly could be varied by supplying power to an electrical heater wound around the copper can. Resistance measurements were made by passing a known constant current through the sample, and measuring the voltage drop to a sensitivity of 0.1 μV.

IV. RESULTS

A comparison of the resistive superconducting-to-normal transitions for sample 1 in the "as-received" state and after an anneal in hydrogen at 1000°C for 8 h is shown in Fig. 1. The transition before heat treatment is quite broad and covers a temperature interval of approximately 0.4°K, indicating that the sample was inhomogeneous. The resistive transition temperature, defined as the temperature at which the sample becomes completely normal in a resistive sense, is found to be 8.25°K, which is in good agreement with the value of 8.22°K found previously for the same type of measurement.[3] Values of the resistivity of this "as-received" sample at 295 and at 9°K are given in Fig. 1, leading to a value of $\Gamma=33$, where Γ is the ratio of the resistivity of the sample at room temperature to the residual resistivity in the normal state. The data show a much sharper transition at 7.71°K for the partially annealed material, which is evidently more homogeneous. The value of Γ in this case increased to 120.

Corresponding isothermal magnetization curves taken

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at 4.2°K before and after the anneal are shown in Fig. 2. The partial annealing and homogenization by the heat treatment drastically decreases the upper critical field H_{c2}, the field at which the magnetization is found to disappear. However, the heat treatment is not sufficient to remove completely the extended defects in the sample responsible for flux pinning, since the magnetization curve is quite irreversible. The transition temperature determined by extrapolation of the $H_{c2}(T)$ data versus temperature gave a value $T_0=7.73\pm0.02$°K, agreeing within the limits of experimental error with the transition temperature measured resistively, and somewhat lower than the value of 8.35°K reported by Trojnar *et al.*[4] for technetium with a greater impurity content. An attempt to heat treat this sample on a tantalum frame in a vacuum furnace (tantalum resistance heater) at a "safe" temperature of 1800°C resulted in an apparent eutectic reaction of tantalum and technetium, resulting in the loss of this sample.

Essentially similar results as described above were obtained in the investigation of sample 2. Some typical isothermal magnetization curves at 4.2°K are shown in Fig. 3 for this sample for several conditions of heat treatment. Intermediate heat treatments at 1500, 1800, and 1900°C were carried out, but for the sake of clarity, the corresponding magnetization curves have been omitted from Fig. 3. As the heat treatment temperature is increased up to 1800°C, it is observed that the area of the hysteresis loop decreases as one would expect, and, in addition, that the value of the upper critical field $H_{c2}(T)$, as determined at a given temperature,

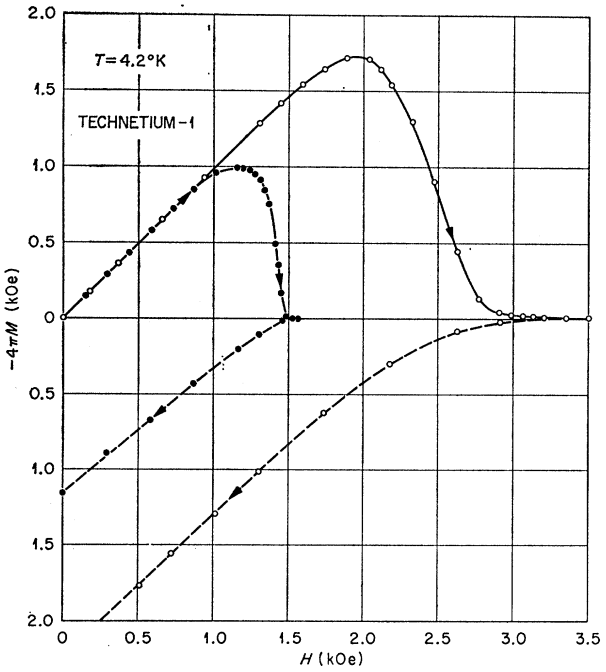

FIG. 2. Isothermal magnetization curves of technetium (sample 1). Open circle—"as received"; closed circle—heat-treated at 1000°C for 8 h.

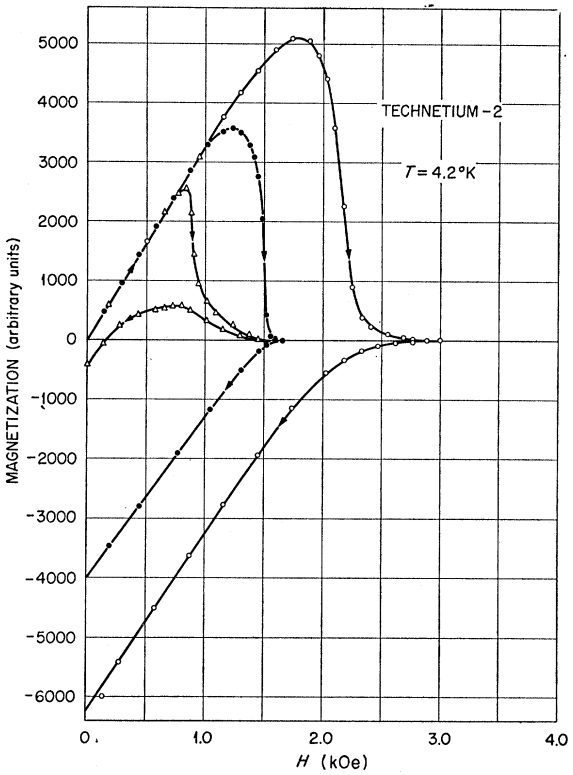

FIG. 3. Isothermal magnetization curves of technetium (sample 2). Open circle—"as received"; closed circle—heat-treated at 1000°C for 8 h; open triangle—heat-treated at 2000°C for 1 h.

decreases without any significant change in the transition temperature. Heat treatments at temperatures of 1800°C or more result in the most nearly reversible magnetization curves we have obtained to date. The magnetization curve shown in Fig. 3, after a 2000°C anneal, is essentially the same as obtained after the 1800°C heat treatment. Polishing the rough matte surface of the sample and subsequent heat treatment did not improve the reversibility.

From the isothermal magnetization data, values of the upper critical field H_{c2} are obtained as a function of temperature, and the transition temperature as determined by the extrapolation of these data is 7.77 ± 0.02°K. The residual resistivity ratio Γ is found to be 97, and indicates that sample 2 is less pure than sample 1. In Fig. 4 a plot of $H_{c2}(t)$ versus the reduced temperature $t=T/T_0$ is shown for sample 2. The value of $H_{c2}(t)$ at 0°K is found by extrapolation to be 2620 Oe while the parameter $-(dH_{c2}(t)/dt)_{t=1}$, which is of interest in the discussion, is determined to be 3250 ± 50 Oe.

As is well known, for a reversible process of magnetization of a superconductor in an external magnetic field H, the thermodynamic critical field $H_c(t)$ is given by

$$\frac{H_c^2(t)}{8\pi}=-\int_0^{H_{c2}(t)} M(H,t)dH,$$

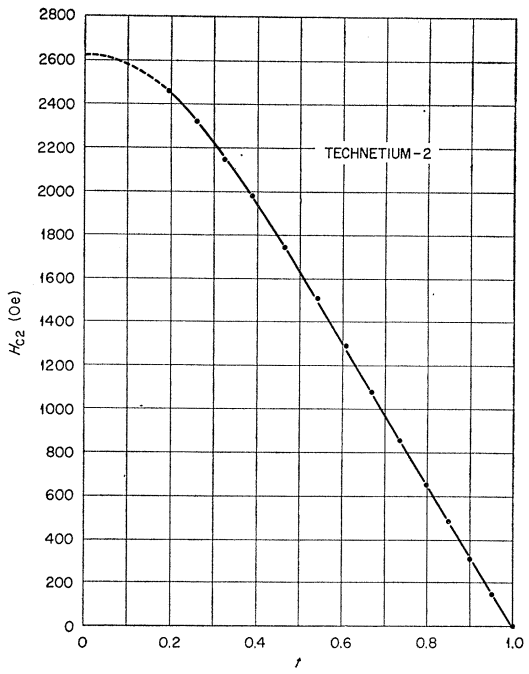

FIG. 4. The upper critical field H_{c2} versus the reduced temperature for technetium.

where $M(H,t)$ is the induced magnetization. In this case, as is commonly observed in investigations of type-II superconductors,[8] the magnetization curves are not completely reversible, and it is thought that flux pinning is due mainly to extended defects remaining after the partial anneal at 2000°C, although the surface sheath[9] and imperfect sample geometry can also contribute to the hysteresis. Thus, by integrating over the isothermal magnetization curves taken in monotonically-increasing field, one overestimates the value $H_c(t)$ by some unknown amount. However, it is useful to obtain these data, as they represent an upper limit to the true thermodynamic field, and can be examined for consistency with the more reliable values of $H_{c2}(t)$. The values obtained by integration are given in the following discussion.

V. DISCUSSION OF RESULTS

A fundamental relation arising from the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory of type-II superconductors[10–13] can be extended to arbitrary temperatures below the superconducting transition temperature, and is given as

$$H_{c2}(t)=\sqrt{2}\kappa_1(t)H_c(t). \tag{1}$$

In this expression, $H_{c2}(t)$ is the upper critical field, $H_c(t)$ is the thermodynamic critical field at a reduced temperature t, and $\kappa_1(t)$ is the dimensionless temperature-dependent Ginzburg-Landau (G-L) parameter. For convenience $\kappa_1(t)$ can be rewritten as $\kappa_1(t)=\kappa_1(1)a(t)$ where $\kappa_1(1)$ is the G-L parameter of the Abrikosov theory, dependent only on electronic parameters of the material, while $a(t)$ describes the temperature variation and assumes the value of one at $t=1$. The uncertainties in the experimental values of $H_c(t)$ due to the observed irreversibilities are such that it is desirable to set aside temporarily discussion of the results in terms of Eq. (1), and consider first the experimental values of the normalized parameter

$$h^*(t)=\frac{H_{c2}(t)}{-(dH_{c2}/dt)_{t=1}}$$

for comparison with recent theoretical calculations.[14] Experimental values of $h^*(t)$ versus t are shown in Fig. 5 for technetium, along with the calculated curve for a type-II superconductor in the clean limit, i.e. $\alpha=0$. Here α is a dimensionless parameter given by $\alpha=0.882\xi_0/l$ where ξ_0 is the Bardeen-Cooper-Schrieffer (BCS) coherence range, and l is the electronic mean free path. The disagreement between the experimental values and the theoretical curves is not surprising since, as Helfand and Werthamer point out,[14] the BCS-Gor'kov model they employ assumes a spherical Fermi surface and weak electron-phonon coupling, and is not valid for all

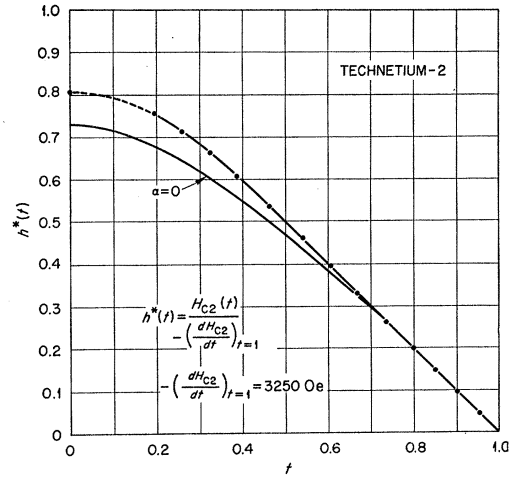

FIG. 5. The parameter $h^*(t)=-H_{c2}(t)/(dH_{c2}(t)/dt)_{t=1}$ versus the reduced temperature for technetium. The curve labeled $\alpha=0$ is that calculated by Helfand and Werthamer (Ref. 14) for a type-II superconductor in the clean limit.

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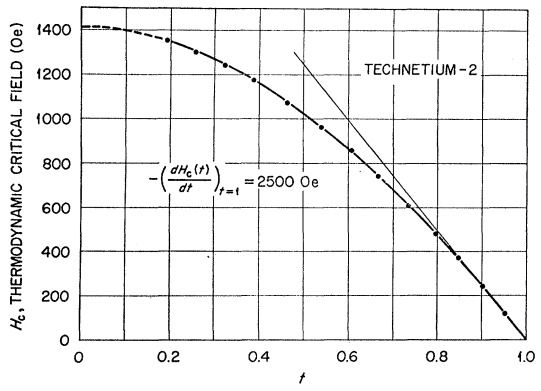

FIG. 6. Experimental values of $H_c(t)$, the thermodynamic critical field versus the reduced temperature for technetium.

superconductors. Thus, in the case of Nb,[15] the observed discrepancy between theory and experiment can be partially accounted for by anisotropy arising from nonlocal corrections to the GLAG theory,[16] but strong coupling effects may also be important.[17] As indicated in the following discussion, the data suggest that technetium is more akin to a BCS superconductor in thermodynamic behavior, so that the observed discrepancy in experimental values of $h^*(t)$ with the calculations is probably mainly due to Fermi-surface anisotropy.

The thermodynamic critical-field values $H_c(t)$ as obtained by integration of the magnetization isotherms are shown in Fig. 6 plotted against the reduced temperature t. The critical field value $H_c(0)$ was obtained by using the approximate relation $H_c(t)=H_c(0)(1-a_2t^2)$, where a_2 is a constant in an extrapolation of the experimental data for the lowest temperatures. This value is $H_c(0)=1410$ Oe and represents an upper limit to the true thermodynamic critical field at 0°K. The slope of the critical field curve at the transition temperature, as determined from the plot, is found to be $-(dH_c(t)/dt)_{t=1}=2500\pm100$ Oe. Plotting the critical field values $H_c(t)$ against the square of the reduced temperature reveals that the data fall below the parabolic temperature dependence shown as the solid straight line in Fig. 7. This negative deviation from parabolic behavior suggests that technetium is essentially a weak electron-coupling superconductor of the BCS type. This is established more quantitatively, by the fact that using the experimental values given above, the ratio $-(dH_c(t)/dt)_{t=1}/H_c(0)$ gives a value of 1.77 for technetium in comparison with the BCS value of 1.76 and the value of 2.00 for the parabolic model. In order to examine the consistency of this value, use is made of the approximate linear relation between the parameters T_0/Θ_D and $\epsilon(0)/kT_0$ for the elemental superconductors, as has been tabulated elsewhere.[8] In these variables, Θ_D is the Debye temperature at 0°K, $\epsilon(0)$ represents one-half of the average value of the superconducting energy gap at 0°K and k is the Boltzmann constant. For technetium, using the value of $T_0=7.77$°K and the value of $\Theta_D=411$°K given elsewhere,[5] one obtains a value of $\epsilon(0)/kT_c=1.795$. The relation proposed by Toxen,[18] which relates the energy gap to the slope of the thermodynamic critical field curve at the transition temperature, can be written as

$$\frac{-(dH_c(t)/dt)_{t=1}}{H_c(0)}=\frac{\epsilon(0)}{kT_0}. \tag{2}$$

This relation, while fortuitous,[19] appears to describe fairly well the data for the elemental superconductors so that for technetium one obtains a value of $-(dH_c/dt)_{t=1}/H_c(0)=1.795$. The agreement between the experimental value and this empirically derived result is quite good in view of the crudeness of the calculation.

The G-L parameter $\kappa_1(1)$ may be determined from the experimental data using

$$\left(\frac{dH_{c2}}{dt}\right)_{t=1}=\sqrt{2}\kappa_1(1)\left(\frac{dH_c}{dt}\right)_{t=1}, \tag{3}$$

which was obtained by differentiating Eq. (1). Substituting the experimental values one finds that $\kappa_1(1)=0.92\pm0.05$. In general, the temperature dependence of the G-L parameter, $a(t)$, can be written as

$$a(t)=\frac{-h^*(t)(dH_c(t)/dt)_{t=1}}{H_c(0)f(t)}, \tag{4}$$

where $H_c(0)f(t)$ represents the temperature-dependent thermodynamic critical field. The function $a(t)$ expected

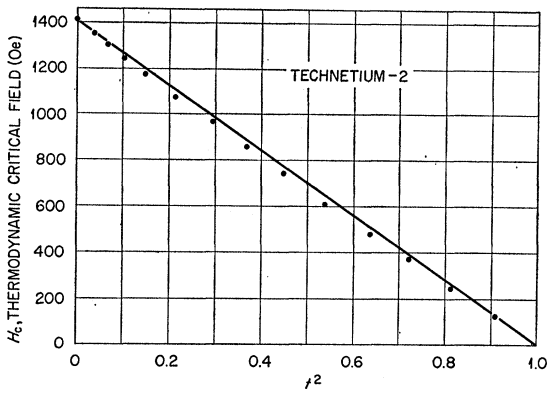

FIG. 7. Experimental values of $H_c(t)$ versus the square of the reduced temperature for technetium.

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for technetium can then be calculated by substituting in Eq. (4), the experimental values of

$$h^*(t), \quad \frac{-(dH_c(t)/dt)_{t=1}}{H_c(0)}=1.77,$$

and the tabulated values of the BCS thermodynamic critical field given by Mühlschegel[20] with the condition that $a(t)$ takes on a value of one at $t=1$. Rewriting Eq. (4) one obtains

$$a(t)=\frac{1.77h^*(t)}{f(t)}, \tag{5}$$

and it is evident that $a(t)$ is independent of both $\kappa_1(1)$ and $H_c(0)$ which are subject to uncertain error. The calculated plot of $a(t)$ is shown in Fig. 8 as the solid curve. The experimental data points

$$a(t)=\frac{H_{c2}(t)}{\sqrt{2}\kappa_1(1)H_c(t)}$$

are also shown for purposes of comparison. At reduced temperatures below $t=0.7$, the experimental values are in fair agreement with the calculated curve, and this consistency would indicate that the experimental values of $\kappa_1(1)H_c(t)$ are reasonably good. At higher temperatures, however, the agreement becomes progressively worse. If one assumes that $\kappa_1(1)$ has been correctly determined, the agreement at lower temperatures with an increasing deviation at higher temperatures suggests that the overestimate of the thermodynamic critical field, arising from integration under the nonreversible magnetization curves, varies somewhat with temperature. This error (in absolute values, never more than 25 Oe) then becomes more significant at higher temperatures resulting in the larger deviations. The electronic-specific-heat coefficient γ as given by the BCS theory[21] is $\gamma=0.170H_c^2(0)/T_0^2$, and using the present experimental data for technetium, a value of $\gamma=4.84$ mJ/g at. deg^2 is calculated. This is somewhat higher than the value $\gamma=4.06$ mJ/g at. deg^2 estimated by Gschneider.[22] In the absence of more reversible magnetization curves for technetium, low-temperature specific-heat measurements could assess the accuracy of these determinations of the thermodynamic critical field and the G-L parameter.

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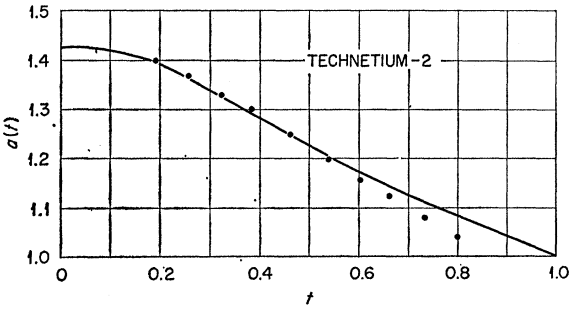

FIG. 8. The temperature dependence of the Ginzburg-Landau parameter, $a(t)$, versus the reduced temperature for technetium. The solid curve has been calculated as described in the text.

VI. SUMMARY OF RESULTS

The superconducting transition temperature of the purer technetium sample studied ($\Gamma=120$) was found to be 7.73 ± 0.02°K. A slightly less pure sample ($\Gamma=97$), which had a transition temperature of 7.77 ± 0.02°K, was studied in more detail. Heat treatment at 2000°C for periods of 1 h yielded the most nearly reversible magnetization curves, from which were extracted the upper critical field values $H_{c2}(t)$ and upper limits to the thermodynamic critical field $H_c(t)$. The temperature dependence of the parameter

$$h^*(t)=\frac{H_{c2}(t)}{-(dH_{c2}(t)/dt)_{t=1}}$$

is shown to be greater than predicted on the basis of the BCS-Gor'kov model,[14] and can be qualitatively understood by taking into account Fermi-surface anisotropy.[16] The negative deviation of the experimental values of the thermodynamic critical field from the parabolic model suggests a behavior similar to that of a BCS superconductor in agreement with an empirically derived estimate. The upper limit to the thermodynamic critical field at 0°K, $H_c(0)$, was found to be 1410 Oe while the G-L parameter was determined as $\kappa_1(1)=0.92\pm0.05$. The experimentally deduced temperature dependence of the G-L parameter is in good agreement with an empirical model at low temperatures, but deviates significantly at higher temperatures. This deviation can be interpreted as a deterioration of the relative accuracy of the measurements closer to the transition temperature, due to the irreversible nature of the magnetization curves.

ACKNOWLEDGMENTS

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