Critical magnetic fields of superconducting films of technetium

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For films of technetium of thickness 55–1600 Å we have measured the critical magnetic fields perpendicular and parallel to the plane of the film, and the resistivity. We have investigated the relation between these quantities and the structure of the specimens and have estimated the change in the electron density of states in the transition to the thin-film FCC modification.

INTRODUCTION

As we have recently reported,[1] in technetium films obtained by ionic evaporation, two phases are observed which are stable at room temperature. Technetium samples of thickness $d < 150$ Å have a FCC lattice with a parameter $a = 3.68 \pm 0.05$ Å. In thicker films a second phase appears with the HCP lattice usual for massive samples ($a = 2.732 \pm 0.002$ Å, $c = 4.381 \pm 0.002$ Å). The amount of the second phase increases with increasing film thickness and for $d \geq 300$ Å amounts to ~100%.

In the present work we have studied the perpendicular and parallel critical magnetic fields $H_c^{\perp}$ and $H_c^{\parallel}$ and the resistivity of films of technetium in the region of thickness[1)] 55–1600 Å. Investigation of the critical magnetic fields is interesting from several points of view: First, there are no data in the literature on the magnetic properties of superconducting technetium films; in addition, it is of interest to trace the connection between the critical fields and the structure of the samples, and finally on the basis of the results on $H_c^{\perp}$ and the residual resistivity ρ_n it is possible to estimate the electronic density of states N(0) for two different modifications of technetium.

I. METHOD

The critical magnetic fields were measured by the resistive method in the temperature region from 4.2 K to the transition temperature of the samples to the normal state. The measurements were made in a cryostat consisting of a chamber inserted into a metal Dewar with a built-in type UIS-1 superconducting solenoid.[2] The chamber was filled with gaseous helium at a pressure 0.5–10 Torr. The temperature was controlled by a heater wound on a copper block with the samples. For protection from temperature instability due to convection currents, the copper block was placed in a copper can.

The block could be rotated about a horizontal axis (Fig. 1). The shaft of the mechanical drive was brought out through a housing with a gasket. The wires leading to the samples and the thermometer were cemented to a tape and bent into a spiral, which provided free rotation of the block by 720°. To reduce the thermal conduction to the samples, the measuring wires were cemented with BF-2 cement to a block at a distance of 50 cm. The measuring current through the samples (0.5–100 μA) was oriented perpendicular to the magnetic field.

The thermometer consisted of an Allen-Bradley carbon resistor, which permitted measurement of the temperature with an accuracy of 0.02 K or better in the range from 2 to 10 K. The fractional increase of the thermometer resistance in a field of 40 kOe at T = 4.2 K was 2%. A correction due to this effect was taken into account.

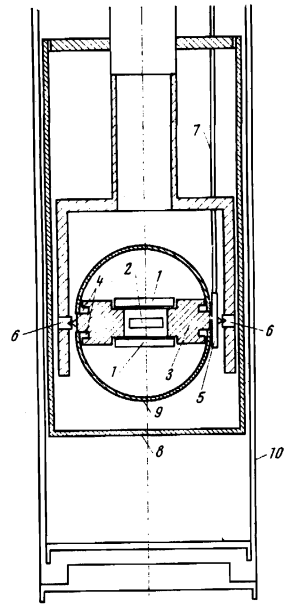

FIG. 1. Lower portion of apparatus for measuring critical magnetic fields of films: 1–sample, 2–thermometer, 3–copper block, 4–heater, 5–worm gear, 6–agate bearings, 7–drive shaft, 8–copper cylinder, 9–cover for block, 10–end of insert in Dewar.

The samples were placed in the center of the superconducting solenoid, whose magnetic field was determined from the current through the solenoid. The solenoid constant H/I was 0.59 kOe/A.

Transitions curves to the superconducting state were recorded for fixed magnetic fields and a slow change of the temperature (with a rate of 0.1 K/min). The transition curves were recorded by means of a two-coordinate recording potentiometer type PDS-021, whose X and Y inputs received error signals from type R348 potentiometers which measured the voltages between potential contacts on the thermometer in the sample.

All measurements of the critical magnetic fields were carried out in films whose edges were cut off by a diamond microknife. This made it possible, in determining the critical fields and resistivity ρ, to avoid errors due to the existence of a penumbra arising during the deposition at the edges of the film. The residual resistivity ρ_n was determined from data on the resistance of the samples above the transition temperature R_n and from the geometry of the samples.

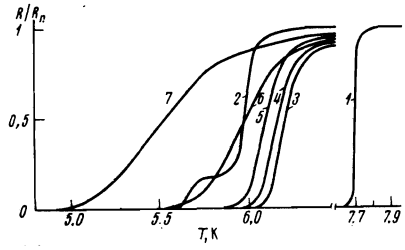

FIG. 2. Transition curves in the case H = 0: 1–d = 1600 Å, 2–d = 160 Å, 3–d = 80 Å, and for films of thickness d = 80 Å in fields: 4–$H^{\parallel}$ = 31.2 kOe, 5–$H^{\parallel}$ = 31.2 kOe, 5–$H^{\parallel}$ = 48.5 kOe, 6–$H^{\perp}$ = 6.02 kOe, 7–$H^{\perp}$ = 17.5 kOe.

The thicknesses of the thickest samples were determined in a multibeam interferometer type MII-11. These thicknesses were then used to calculate the rate of deposition. The thicknesses of the remaining samples were calculated from the rate and time of deposition. The rate of deposition was maintained constant with an accuracy of 4% or better.

II. RESULTS

1. Transition Curves in Zero Magnetic Field

Typical transition curves in zero magnetic field are shown in Fig. 2. For the sample with d = 160 Å they had a step shape due to the presence of two phases in the sample. The width of the transition[2)] at zero field $\Delta T(0)$ varied from 0.03 (for d = 1600 Å) to 0.37 K (for d = 55 Å). These values are one to two orders of magnitude higher than the fluctuation widths of the transition calculated from the theory of Larkin and Aslamazov.[3]

2. Perpendicular Critical Magnetic Fields

In a perpendicular magnetic field the transition curves are broadened; however, as in zero field, the middle part of the curves remains linear (Fig. 2). The width of the transition $\Delta T(H)$ increases with increasing field, and the function $\Delta T(H)$ for all samples is close to linear.

In the case of an extended transition curve, the question arises of what point on this curve is to be considered to correspond to the critical field. In Fig. 3 we have shown curves of the temperature dependence $H_c^{\perp}$ for a sample with d = 80 Å. The temperature corresponding to the experimental points in this figure was determined from the transition curves R(T) for constant H in the following way: for curve 1–from the point of intersection of the extension of the central straight portion with the horizontal, $R/R_n = 1$, i.e., from the "end" of the transition curve from the superconducting state to the normal state; for curve 2–from the point where $R = R_n/2$, i.e., from the "middle' of the transition curve. In what follows we will designate values of $H_c^{\perp}(T)$ determined from the end and middle of the transition curve respectively as[3)] $H_{c,n}^{\perp}(T)$ and $H_{c,1/2}^{\perp}(T)$.

For the films of thickness 1600, 640, 320, 160, and 55 Å, the dependence $H_{c,n}^{\perp}(T)$ is linear in the temperature region studied (Fig. 4), and the deviation of the experimental points from a straight line does not exceed the experimental error; for the films of thickness 110 and 80 Å in the immediate vicinity of T_c (for $T_c - T \lesssim \Delta T(0)$) a weak departure of this dependence from linearity is observed (Figs. 3 and 4). A linear dependence of $H_{c,1/2}^{\perp}(T)$ is observed for all films over the entire temperature region studied.

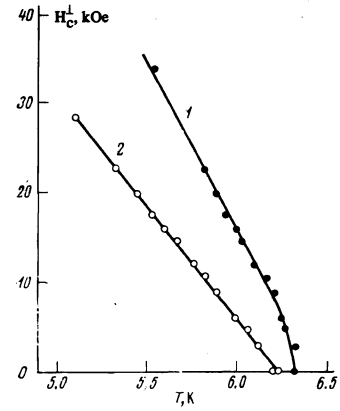

FIG. 3. Temperature dependence of perpendicular critical fields for film with d = 80 Å: curve 1–$H_{c,n}^{\perp}$, 2–$H_{c,1/2}^{\perp}$.

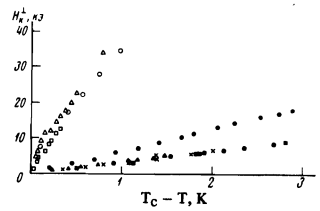

FIG. 4. Temperature dependence of $H_{c,n}^{\perp}$: ●–d = 1600 Å, ■–640 Å, X–320 Å, ▲–160 Å, ○–110 Å, △–80 Å, □–55 Å.

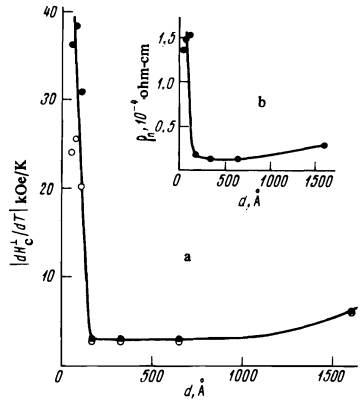

FIG. 5. Dependence on sample thickness a) of the quantity $|dH_c^{\perp}/dT|$: ●–$|dH_{c,n}^{\perp}/dT|$, ○–$|dH_{c,1/2}^{\perp}/dT|$; b) resistivity.

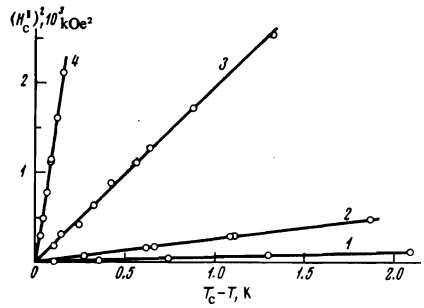

FIG. 6. Temperature dependence of parallel critical fields: 1–d = 640 Å, 2–320 Å, 3–160 Å, 4–55 Å.

The derivatives $|dH_c^{\perp}/dT|$ near T_c, determined by the two different methods, i.e., $|dH_{c,1/2}^{\perp}/dT|$ and $|dH_{c,n}^{\perp}/dT|$, are shown in Fig. 5a as a function of sample thickness. In determining these quantities we used the linear portions of the functions $H_c^{\perp}(T)$.

3. Parallel Critical Fields

The transition curves in a parallel magnetic field do not change their shape and width over a rather wide temperature region near T_c (Fig. 2). For all samples studied $(H_c^{\parallel})^2$ is directly proportional to $\Delta T = T_c - T$ for small ΔT (Fig. 6). As a result of the constancy of the shape of the transition curves, the slope of $(H_c^{\parallel})^2$

as a function of temperature does not depend on what point in the transition curve $H_c^{\parallel}$ is defined as. We took the temperature corresponding to $H_c^{\parallel}$ as that for which $R = R_n/2$.

4. Resistivity

The residual resistivity ρ_n of films of various thicknesses is shown in Fig. 5b. Note the strong correlation between ρ_n and $|dH_c^{\perp}/dT|$. In the transition from the HCP lattice to FCC, beginning with d ~ 100 Å, a sharp rise of ρ_n and $|dH_c^{\perp}/dT|$ occurs. Here both of these quantities change by an order of magnitude: While for d = 160–640 Å, we have $\rho_n = (0.1\text{–}0.2) \times 10^{-4}$ ohm-cm and $|dH_c^{\perp}/dT| = 3.1\text{–}3.3$ kOe/K, on the other hand for d = 55–110 Å we have $\rho_n = (1.3\text{–}1.5) \times 10^{-4}$ ohm-cm and $|dH_{c,n}^{\perp}/dT| = 31\text{–}38$ kOe/K. The ratio ρ_{300}/ρ_n varies from 2.0–3.2 for films with $d \geq 160$ Å down to 0.95–0.96 for films with $d \leq 110$ Å.

III. DISCUSSION

Tinkham[4, 5] showed that the value of the perpendicular magnetic field at which the superconducting transition occurs in thin films of type I superconductors and in films of arbitrary thickness of type II superconductors[4)] coincides with H_{c2}. The extent of the transition leads, however, to some uncertainty in the values of the critical field. The cause of the extension of the transition curve in magnetic field may be both the nonuniformity of the samples and the effective resistance associated with motion of Abrikosov vortices. In the first case the choice of the point on the transition curve for determination of H_{c2} depends on the nature and distribution of nonuniformities in the sample. In the second case the theoretical results of refs. 7–10 provide a basis for taking as H_{c2} the field obtained by extrapolation of the R(H) curves[5)] to $R = R_n$. At the same time Bergmann[11] presents arguments in favor of determining H_{c2} from the field $H_{c,n}^{\perp}$.

The temperature dependence of H_{c2} for superconductors with a small mean free path ($l \ll \xi_0$), according to the calculations of Maki[12] and de Gennes,[13] should be (within ~2%) linear over a rather wide range of temperatures near T_c (down to $T/T_c \sim 0.7$). As already noted, for our samples a linearity of $H_{c,n}^{\perp}(T)$ and $H_{c,1/2}^{\perp}(T)$ is observed in the temperature region studied, at least for $T_c - T \gtrsim \Delta T(0)$.

The proportionality observed for our samples between $(H_c^{\parallel})^2$ and $T_c - T$ near T_c agrees with the Ginzburg-Landau formula[14] for $H_c^{\parallel}$:

$$H_c^{\parallel} = \sqrt{3}\varphi_0/\pi d\xi_T. \tag{1}$$

1. Relation of Critical Magnetic Fields and Resistivity to Sample Structure

The strong correlation between the variation of ρ_n and $|dH_c^{\perp}/dT|$ with thickness of the films can be explained by means of the relation

$$|dH_{c2}/dT|_{T=T_c} = 2.55 ke c \rho_n N(0), \tag{2}$$

which follows from the theory of Gor'kov[15] for the case $l \ll \xi_0$. Here N(0) is the electronic density of states at the Fermi surface, l is the average mean free path of electrons, and ξ_0 is the coherence length:

$$\xi_0 = 0.18\hbar v_F/kT_c, \tag{3}$$

where v_F is the Fermi velocity. Expression (2) was obtained by the combined use of the following formulas:

$$H_{c2} = \varphi_0/2\pi\xi_T^2; \tag{4}$$

$$\xi_T = 0.85[l\xi_0(T_c - T)/T_c]^{1/2}, \quad T_c - T \ll T_c, \quad l \ll \xi_0, \tag{5}$$

$$1/\rho_n = {}^2/_3 e^2 N(0) l v_F, \tag{6}$$

where φ_0 is the quantum of magnetic flux and ξ_T is the temperature-dependent coherence length.

The variation of the quantities $|dH_c^{\perp}/dT|$ and ρ_n in the transition from HCP to a FCC lattice is determined by the decrease in the product $l\,v_F$; N(0) changes weakly (detailed data on N(0) will be discussed below). The product lv_F can change as the result of two factors. A sharp decrease in the grain size (from a ~ 10 000 Å for films with $d \gtrsim 300$ Å to $a < 100$ Å for films with $d \lesssim 100$ Å), which accompanies the transition from one modification to the other, probably leads to the fact that as a result of scattering at grain boundaries l also decreases sharply.

In addition, the value of the ratio ρ_{300}/ρ_n for films with $d \lesssim 100$ Å (0.95–0.96) provides a basis for suggesting that the resistivity of these samples is affected by intercrystalline barriers. In this case, as shown by Abeles et al.,[16] the applicability of the theoretical expressions for H_{c2} for $l \ll \xi_0$ remains in force if the condition $\xi_T \gg b$ is satisfied, where b is the distance between the barriers. For the samples considered, a characteristic value for b can be considered the grain size ($b \sim a < 100$ Å), so that the inequality $\xi_T \gg b$ is satisfied in the temperature region corresponding to fields $H_c^{\perp} < 30$ kOe. In this case l, the effective mean free path, is expressed in terms of b and the transmission coefficient of the barriers.

From data on $H_c^{\perp}$ and $H_c^{\parallel}$ it is possible to determine the thickness of the samples:

$$d_H = (6\varphi_0 H_c^{\perp}/\pi)^{1/2}/H_c^{\parallel}. \tag{7}$$

This relation is obtained by elimination of ξ_T from Eqs. (4) and (1). The difference in the values of d_{opt} (obtained by an optical method) and d_H is small. This indicates the correctness of use of the theoretical relations discussed for our samples. It is possible that obtaining somewhat reduced (by about 30%) values of d_H for thick films ($d_{opt} = 320\text{–}1600$ Å) is due to the nonuniformity of the film thickness. Since $H_c^{\parallel} \sim 1/d$, the parallel critical fields are determined by the minimum thicknesses. On the other hand, the optical method gives the thickness averaged over some microscopic part of the film. The increase of d_H for thin films may be due to smoothing of the surface relief of the film, originating from the fact that for the films of thickness 55 and 80 Å the ratio of grain size to sample thickness is two orders of magnitude lower than for the thick samples.[1]

2. Electronic Density of States

Golyanov et al.[17] have suggested use of Eq. (2) for evaluation of N(0) in films with a small mean free path. It should be noted that the small mass of the film samples hinders measurement of their heat capacity for the purpose of determining N(0).

The dependence of the ratio $N(0)/N_m(0)$ on film thickness is shown in Fig. 7. Values of N(0) were determined from Eq. (2) by several means: 1) In calculation of ρ_n we used the optical thickness d_{opt}, and for $H_c^{\perp}$ we took respectively $H_{c,n}^{\perp}$ and $H_{c,1/2}^{\perp}$; 2) we as-

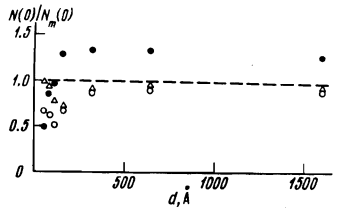

FIG. 7. Dependence of electronic density of states obtained by means of Eq. (2) from the thickness of the samples for different means of determining $H_c^\perp$ and d: 1) $d = d_{opt}$, △–$H_c^\perp = H_{c,n}^\perp$, ○–$H_c^\perp = H_{c,1/2}^\perp$; 2) ●–$d = d_H$, $H_c^\perp = H_{c,1/2}^\perp$.

sumed $d = d_H$ and $H_c^\perp = H_{c,1/2}^\perp$. The value of the electronic density of states for pure massive technetium, $N_m(0) = 1.02$ eV^{-1}-atom^{-1}, calculated from data on the thermodynamic critical field at T = 0 and the transition temperature, was taken from the work of Sekula, Kernohan, and Love.[6] The error in determination of N(0) evidently does not exceed 10%.

The correction for the finiteness of the ratio $1/\xi_0$, determined on the basis of the theoretical results of Gor'kov[15] (see also ref. 18), amounts to 8–16% for films of thickness 320–1600 Å, but is negligible for films of thickness $\lesssim$ 100 Å. We note that Eq. (2) is valid on the assumption of weak coupling. Technetium belongs to the case of intermediate coupling ($T_c/\Theta_D = 0.023$), and we can assume that the correction for strong coupling will be insigificant.

Use of the optical thickness in determination of N(0) seems more reasonable, since d_{opt} is a quantity averaged over some macroscopic portion of the film, while the magnetic thickness may be determined by thin portions of the film. For thick films with an HCP lattice (d = 320–1600 Å), N(0) coincides with $N_m(0)$ regardless of the means of determination of $H_c^\perp$ (since the transition curves for these samples are comparatively sharp) if the optical thickness is used. When the magnetic thickness is used for these films, N(0) exceeds $N_m(0)$ by about 30%.

For the films of thickness 55 and 80 Å, which have a FCC lattice, as a result of the strong extension of the transition curves, significant variations of N(0) are observed regardless of how $H_c^\perp$ is determined. If the optical thickness is used, the $N(0)/N_m(0)$ remains close to unity for $H_c^\perp = H_{c,n}^\perp$ and decreases to ~0.7 for $H_c^\perp = H_{c,1/2}^\perp$. When the magnetic thickness is used, $N(0)/N_m(0)$ drops to ~ 0.5.

In determination of N(0) for the films of thickness 55 and 80 Å, it was taken into account that the density of material calculated from the electron-diffraction data of ref. 1 for technetium with a FCC lattice is 13% higher than the density of technetium with an HCP lattice. It should be noted that in the region of two-phase composition (d = 110 and 160 Å), nonuniformity of the samples apparently leads to a large error in determination of N(0). The uncertainty contributed by the lack of sharpness of the transition curves in the films with an FCC lattice and the existence of some discrepancy between the optical and magnetic thicknesses prevents us from drawing any conclusions as to the change of N(0) in a structural transition. However, even when this uncertainty is taken into account, we reach the conclusion that in the transition from the massive hexagonal modification of technetium to the thin-film cubic modification, the density of states N(0) either remains constant or decreases.

In conclusion the authors thank N. A. Chernoplekov and B. N. Samoĭlov for their interest and their attention to this work, R. O. Zaĭtsev for discussions, A. P. Demidov and E. A. Zhitnitskiĭ for assistance in preparing the samples and carrying out the experiment, and V. A. Dravin for taking part in building the cryostat insert.

[1)]For protection from oxidation, the freshly prepared technetium samples were immediately covered in the same apparatus with a film of synthetic diamond of thickness 40 Å.

[2)]The width of the transition was taken as the temperature interval between the points of intersection of the straight line obtained by extension of the central straight portion of the transition curve with the horizontal lines R = 0 and $R = R_n$. An exception is the film of thickness 160 Å, for which the transition width $\Delta T(0)$ was determined as the temperature interval between the beginning of the first step and the end of the second step, and amounted to 0.42 K.

[3)]For the sample with the step transition $H_{c,1/2}^\perp$ and $H_{c,n}^\perp$ refer the sharper jump in the R(T) curve.

[4)]Pure massive technetium is a superconductor of type II [6] with H = 0.92.

[5)]We have replotted the families of R(T) curves for constant H into families of R(H) curves for various T and found that the derivatives $|dH_c^\perp/dT|$ for the critical fields determined by extrapolation of the central part of the R(H) curves to $R = R_n$ practically coincide with $|dH_{c,n}^\perp/dT|$ for samples with d = 160–1600 Å, while for samples of thickness 55–100 Å they are 10–20% lower than $|dH_{c,n}^\perp/dT|$.

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118