T_c suppression and critical fields in thin superconducting Nb films

J. H. Quateman*
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 27 January 1986)

Thin Nb films from 30 to 150 Å thick have been electron-beam evaporated onto sapphire substrates with aluminum overlayers, then deposited to protect the surface. T_c's and magnetoresistance were found to be consistent with localization models, and measured parallel critical fields fit a generalized Ginzburg-Landau theory. Perpendicular critical fields, however, were found to have an anomalous curvature near T_c. These results, we believe, are due to the disorder of the film and have also been seen in other systems.

I. INTRODUCTION

Thin films of transition-metal elements have been of interest for many years not only because of their intrinsic interest as high-T_c materials, but also because their robust materials properties make them a good candidate for superconducting electronics.

A major stumbling block, however, in the use of these materials has been degradation of the superconductivity in the surface layer resulting in poor tunnel junctions and reduction of T_c in thin films. This effect was discussed in the early 1970s by Ganqvist and Claeson[1] and Strongin, Thompson, Kammerer, and Crow[2] in terms of a proximity effect between the superconductor and a surface sheath of suppressed superconductivity, due possibly to a decrease in the electron density at the surface. In the late 1970s and early 1980s it was realized that the transition-element suboxides had a prominent role in suppressing T_c. In 1981 Rowell, Gurvitch, and Greek[3] investigated the role of Nb suboxides on the (poor) quality of Nb tunnel junctions. They deposited an aluminum overlayer and confirmed via tunneling measurements that the niobium oxide formation was suppressed and that the Al_2O_3 on the surface formed a good oxide barrier. Later x-ray photoemission spectroscopy (XPS) studies corroborated this.[4] This technique of depositing protective overlayers is not new,[5,6] but not until recently has the potential of this technique to study the properties of thin films of transition elements and compounds been realized.

In the late 1970s and early 1980s it was also realized that weak localization and interaction effects play an important role in the properties of thin superconducting films. In particular, the repulsive Coulomb interaction is enhanced due to two-dimensional effects and reduced mobilities. In 1984, Graybeal and Beasley[7] performed experiments on Mo-Ge films and found good agreements between their T_c suppression and the model Maekawa and Fukuyama based on interaction effects in 2D disordered systems. This work is being extended at Stanford to niobium films by Park,[8] who in his preliminary results confirms this behavior in transition elements.

We have made niobium films in order to concentrate on the effects of reduced dimensionality and disorder on the critical fields. This experiment was originally contemplated as a first step in making $Nb/Al_2O_3/Fe$ tunnel junctions in order to measure the spin-orbit scattering rate by the technique of spin-polarized tunneling. The results of that work will be presented at a later date.

II. EXPERIMENTAL METHODS

A. Fabrication

Niobium films using 99.999%-pure Nb were electron-beam evaporated onto $0.64\times1.27\text{-cm}^2$ sapphire substrates heated to 700 °C. A Mo mask was placed over the substrates during evaporation to produce a well-defined pattern for measuring resistance per square. Base pressures before evaporation were in the mid-10^{-8}-torr range and rose to 2×10^{-7} torr during the evaporation. Residual gasses consisted mainly of H_2, CO, and CO_2. Evaporation rates were regulated to 3 Å/sec and film thicknesses were determined by calibrated quartz-crystal monitors. After the Nb evaporation pressures returned to the mid 10^{-8} torr in less than 1 min, and after the substrate had cooled to 200 °C (approximately 7 min), 20–75 Å of aluminum were subsequently evaporated to protect the Nb surface.

B. Measurement Techniques

The transition temperature T_c was measured by a four-terminal dc resistance technique with the sapphire substrates clamped to an oxygen-free high-conductivity copper block which had a calibrated Lake Shore Cryotronics model No. DT-500 silicon diode thermometer[9] imbedded in it. The block was enclosed in a stainless-steel can with He exchange gas and lowered into a liquid-helium storage Dewar.

Critical-field measurements were made in a 15-T Bitter magnet[10] using either a one-shot ^{3}He refrigerator in which the sample is immersed in the liquid ^{3}He, or for higher temperatures a variable-temperature Dewar system[10] using a capacitance thermometer, which has negligible magnetoresistance, to regulate the temperature in the magnetic field. Again, transitions were measured using the four-terminal dc technique. The current through the samples was 10 μA, and this value was reduced by a factor of 10 in

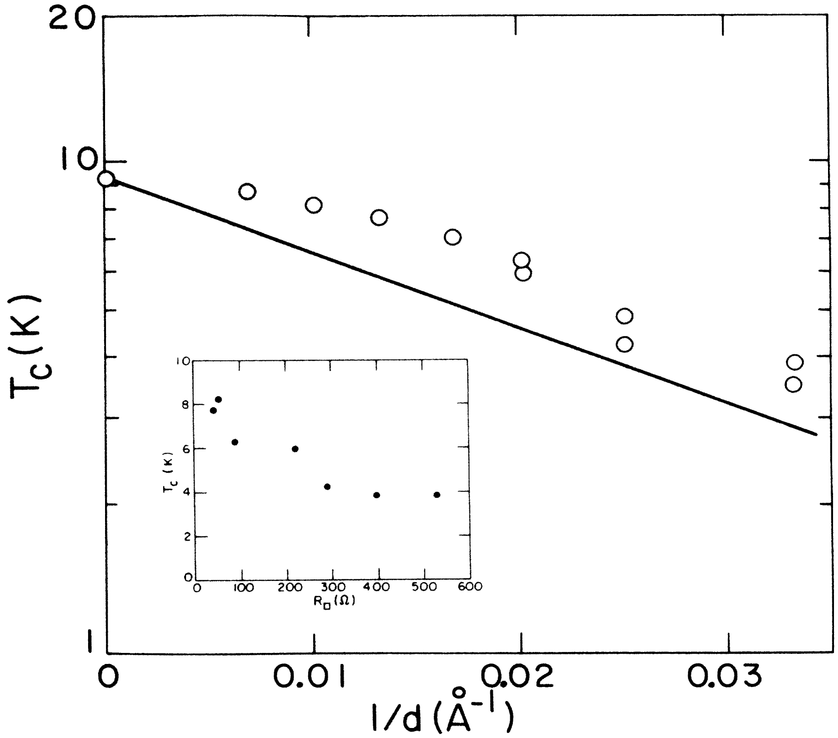

FIG. 1. T_c vs 1/thickness. Solid line is the data of Wolf *et al.* (Ref. 11).

each run to ensure that there was no self-heating. Magnetoresistance measurements were made with a three-terminal ac bridge technique, using a Princeton Applied Research 124 lock-in amplifier. Changes in resistance of five parts in 10^6 were easily observed above the noise.

C. Results and Discussion

Figure 1 shows T_c vs $1/d$, where d is the Nb film thickness. Also plotted are the data of Wolf, Kennedy, and Nisenoff.[11] By slight variation of the substrate temperature or base pressure during the evaporation, the resistance per square could be made to vary greatly while only slightly affecting T_c (see inset, Fig. 1). Note that for these films the resistance per square $R_\square$ for a given thickness is much greater than that of Park.[8] Also, where T_c as a function of d was extensively repeatable, $R_\square$ as a function of T_c was not. It appears that the mean free path l that affects the superconductivity (through ξ) is not the same quantity one extracts from the resistivity in these films. It is not clear yet what material properties are controlling ρ, only that T_c's and H_c's are not very sensitive to ρ or $R_\square$, but are to d. Resistance ratios also varied among samples of the same thickness with no correlation with T_c, though not as severely as $R_\square$ (see Table I). The $1/d$ dependence of T_c is consistent both with a simple proximity-effect model[12] and with localization models.[13] To gain some insight into which of these mechanisms is causing the suppression of T_c we varied the Al overlayer thickness and found that the values of T_c of the films were independent of the Al overlayer average thickness from 10 to 75 Å, suggesting that all the Al is oxidized as it fills grain boundaries, which is consistent with XPS studies done by Kwo, Wertheim, Gurvitch, and Buchanan.[4] We also performed XPS measurements on our films and found no Al metal or niobium oxides present, only Al_2O_3. In addition, our XPS

TABLE I. Material properties of superconducting Nb films on sapphire with protective aluminum overlayers.

d (Å)	T_c (K)	ρ ($\mu\Omega$ cm) at 4 K	$R_\square$ at 4 K (Ω)	R(4.2 K)/R(300 K)	C_f[a]	b_f[b]
30	3.9	160	533	1.15	0.28	2.0
30	3.6	680	2267	1.6	0.28	2.2
50	6.25	44	88	1.5	0.25	0.8
50	6.0	111	222	1.2	0.65	1.0
75	7.7	33	44.2	1.9	1.8	2.0
100	8.2	52	51.6	2.4	2.4	2.0

[a] $b_f = \hbar/3\tau_{so}\Delta_0$.

[b] $c_f = D(ed)^2\Delta_0/6\mu_B$, where $D = V_F l/3$.

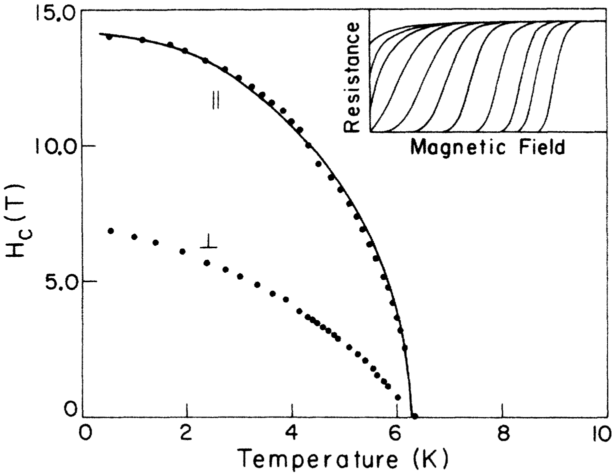

FIG. 2. Critical-field curves for 50-Å Nb film. The solid line is a fit to WHH theory for parallel critical fields. Inset is the resistance isotherms used to calculate the perpendicular critical fields.

depth profile studies showed no Nb oxides between the sapphire substrate and the Nb films. Since XPS is sensitive to only about 1% concentration in the volume it samples, there could still be Nb oxides, and hence, proximity effects present. However, quasiparticle tunneling measurements showed no sign of a proximity knee and very symmetric conduction curves above the gap indicating the absence of Nb suboxides on the top surface.

Magnetoresistance measurements on the 50-Å film show a positive magnetoresistance $\Delta R/R = 2.5\times10^{-4}$ in a 3.5-T field, consistent in magnitude with weak localization with significant spin-orbit scattering (weak antilocalization).

These data lead us to the qualitative conclusion that weak localization is playing an important role in these films. Looking at resistance isotherms for the 50-, 75-, and 100-Å films (insets, Figs. 2, 3, and 4) notice the lack of structure in the transitions indicating a homogeneous film. For the 30-Å films the transition becomes too broad to be able to make any conclusions about the homogeneity.

H_c was determined by both the 50% normal resistance and by taking the midpoint in the field between the 10% and 90% resistance points. For films less than 50 Å these two methods gave slightly different values of H_c but did not affect the shape of the H_c curves. The 50% points were used to plot the critical-field curves. Parallel and perpendicular critical-field curves are shown for 50-, 75-, and 100-Å films in Figs. 2, 3, and 4.

The parallel critical fields behave as in the thin-film limit of the Ginzburg-Landau theory (a square-root-T behavior near T_c). We have made fits to the data by using a Fulde-Maki modified Werthamer, Helfand, and Hohenburg (WHH) theory[14,15] which takes into account spin-orbit scattering (solid lines in Figs. 2, 3, and 4). The data fit reasonably well. Table I shows b_f, the spin orbit scattering term, and C_f, the Maki orbital depairing parameters from the best fits. The parallel-critical-field data are what one would expect from BCS theory in the thin-film limit.

However, as we turn our attention to the perpendicular critical field, we see a marked curvature in $H_{c\perp}$ near T_c. This does not at all fit in the Ginzburg-Landau theory where one would expect a linear dependence in $H_{c\perp}$ near T_c. The initial slope of $H_{c\perp}$ is approximately constant at 2 T/K for the 50–100-Å films. As the films get thinner the apparent curvature decreases because $H_{c\perp}$ increases due to the reduced mean free path. The data cannot be fitted to a WHH-based theory for any fitting parameter as the equations do not allow for such high-T curvature, even for the 50-Å film. This anomalous result remains a mystery and is not due to material problems considering how well parallel critical fields can be fit. It does not seem to be just a bending of the $H_{c\perp}$ curve due to the suppression of T_c in light of the well-behaved parallel-critical-field curves. We believe this is a localization effect, as critical

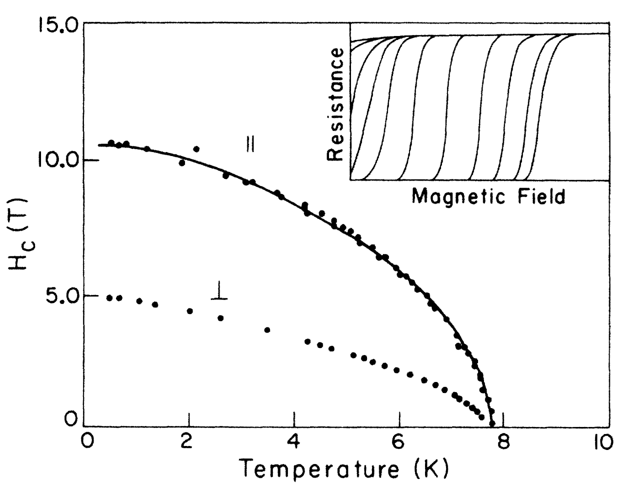

FIG. 3. Critical-field curves for a 75-Å Nb film. Solid line is a fit to WHH theory. Inset is resistance isotherms for determining $H_{c\perp}$.

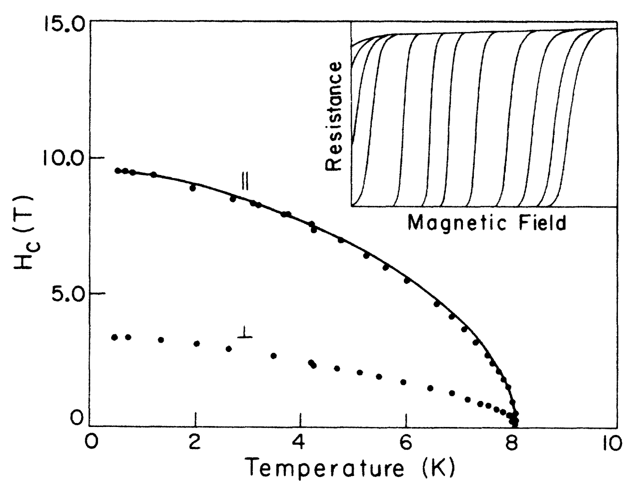

FIG. 4. Critical-field curves for a 100-Å Nb film. Solid line is a fit to WHH theory. Inset is resistance isotherms for determining $H_{c\perp}$.

fields with this curvature have also been seen in the Mo-Ge films of Graybeal and Beasley,[7] where they have significant control over $R_\square$ and ρ and have fit T_c vs $R_\square$ to localization and interaction theories. We also point out the similarity of the shape of these critical-field curves to some heavy-fermion materials, in particular UBe_{13}, a material with strong disorder. This is, of course, the only similarity between the two systems.

To gain further insight into the critical fields we examine H_c vs d at $T=0$. Assuming $l \sim d$, the Ginzburg-Landau equations for films become

$$H_{c\parallel} \approx \frac{H_c \lambda_L \varepsilon_0}{d^{3/2}}, \quad H_{c\perp} \approx \frac{\phi_0}{2\pi\xi^2} \approx \frac{\phi_0}{2\pi\xi_0 d} .$$

Although it is not apparent that in our case $l \sim d$ (since ρ certainly is not proportioned to $1/d$), the mean free path l one extracts from ρ is not the number to use for $\xi = \sqrt{l\xi_0}$ since T_c and H_c are insensitive to ρ in our films for a given d. We use $l \sim d$ as a first-step model to see if we gain any insights. If one plots the critical field as a function of d as in Fig. 5, one gets a straight line for $d \gtrsim 50$ Å. It first seems that the Ginzburg-Landau equations fit the data for films thicker than 50 Å in spite of our assumption of $l \sim d$. However, this is assuming ξ_0 is constant. The T_c of the films change with thickness and so should $\xi_0 \sim V_F/T_c$. If we put the T_c dependence into the equations the data do not fit a straight line anymore. These results are very interesting and not understood. They may give some insight into localization and T_c suppression.

At thicknesses less than 50 Å, H_c starts to slowly decrease. The films may be clustering and/or not be of uniform thickness. In any case, there seems to be something different occurring below 50 Å.

In conclusion, we have made thin niobium films from 30 to 150 Å in which weak localization exists. These films give anomalous $H_{c\perp}$'s which have not yet been explained.

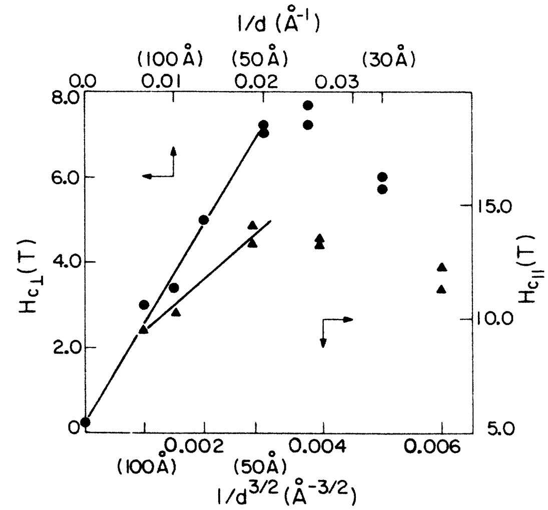

FIG. 5. Parallel and perpendicular critical fields at $T=0.5$ K plotted to compare with Ginzburg-Landau theory. Lines are guides for the eye. See text for details.

ACKNOWLEDGMENTS

This work was supported by the U.S. Air Force Office of Scientific Research Contract No. F49620-82-K-0028. The author would like to thank Dr. R. Meservey, Dr. J. S. Moodera, and Dr. P. Tedrow for their discussions and insight. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation.

*Present address: Raytheon Company, Research Division, 131 Spring Street, Lexington, MA 02173.

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