Thickness dependence on the superconducting properties of thin Nb films

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The thickness dependence of the superconducting properties of Nb films has been studied by resistance and ac magnetic susceptibility measurements. The film thickness was varied from 825 to 200 Å by anodizing a single dc sputtered film in order to minimize any sample-to-sample preparation variations. For films 400 Å thick and greater, the normal-state resistivity at 10 K is constant and the suppression of the superconducting transition temperature T_c with decreasing thickness is explained in terms of both the proximity effect and weak localization. The magnetic susceptibility results show that the diamagnetic transition broadens with decreasing thickness and increasing ac fields as a result of the effective fields becoming greater than the critical field H_{c1} of Nb.

I. INTRODUCTION

It has been found that the superconducting transition temperature T_c for Nb films as well as for other transition-metal films can be severely reduced as the film thickness is decreased. Typically the transition temperatures have been found to decrease inversely with the thickness.[1–11] Initially this suppression of T_c was discussed in terms of a proximity effect between the superconductor and a normal-metal surface layer[2,5,7] on either surface of the film. In the limit of films thinner than the superconducting coherence length, the transition temperature T_c was predicted[12] to follow

$$\ln[T_c/T_{c0}] = -2a/N(0)Vd \ , \tag{1}$$

where d is the thickness of superconducting film, a is the nonsuperconducting surface layer thickness on each side of the film, and $N(0)V$ is the bulk interaction potential. Equation (1) clearly shows the observed suppression in T_c with $1/d$ as reported in earlier work. In the early 1980's, it was further realized that weak localization and interaction effects could also play an important role in the properties of thin superconducting films. This is especially important in films which are in the dirty superconductor limit. For amorphous Mo-Ge films, which satisfy these conditions, Graybeal and Beasley[13] performed T_c vs d experiments and successfully explained the suppression of T_c on $1/d$ by the localization model of Maekawa and Fukuyama.[14] According to this model, the localization reduces T_c because the Coulomb repulsive interaction is enhanced and the electronic density of states is depressed. Subsequent work on amorphous W-Re films[15] and thin Nb films[10,11] provided additional support for the effect of localization on the suppression of T_c.

However in many experiments on transition-metal superconducting films, the suppression of T_c on thickness may also be attributable to a bulk resistivity effect (a broadening of the density of states) in addition to the proximity effect and localization. The separation of these effects is further complicated by the T_c properties being dependent upon the film deposition parameters as pointed out by several groups.[2,8,10] Thus deposition variations even in the same deposition run can lead to T_c variations from sample-to-sample and obscure the thickness dependent properties. Moreover, Park and Geballe[10] have shown that the T_c of even *bulk* niobium films is very sensitive to the deposition conditions including the residual gases in the deposition process and the deposition rate. Thus an alternative technique involving a single-film deposition could be beneficial in performing electrical and magnetic property characterizations as a function of film thickness. We have utilized an anodization technique to vary the thickness of a single dc sputtered Nb film from 825 to 200 Å and thus minimized the sample-to-sample variation in deposition conditions. The constant residual (normal-state) resistivity of approximately 25 $\mu\Omega$ cm for film thicknesses greater than 400 Å indicated that the films are essentially identical for these thicknesses as well as being unaffected by the anodization process and that they are in the dirty superconductor limit. The overall depression of T_c below the value of 9.2 K for bulk Nb is due to the bulk resistivity effect and the strong suppression of T_c with decreasing thickness is attributed to a combination of the proximity effect and localization. Similarly the magnetic susceptibility shows a suppression of the flux exclusion and a broadening of the transition width with increasing magnetic field and decreasing film thickness.

II. EXPERIMENTAL DETAILS

A rectangular Nb film (7.6×2.5 cm^2) of 825 Å thickness was deposited by dc sputtering onto a glass substrate which was precleaned using a series of acetone, alcohol, and distilled water washes. This precleaning procedure was followed by suspending the substrate in the warm vapor of an isopropyl alcohol bath to ensure a contamination-free surface. The deposited Nb film is then partially immersed in an electrolytic solution containing a mixture of 15.6-g ammonium pentaborate, 112-ml ethylene glycol, and 76-ml of distilled water.[16] The film is utilized as the anode via electrical contact to the

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film surface above the electrolyte and gold wire is utilized as the cathode. For a constant current of 10 A/m^2, the cell voltage increases linearly with time such that 7.4±0.8 Å of Nb are anodized for each volt across the cell. The variation of thickness over the entire unanodized Nb film was subsequently determined to be less than 2 Å as measured by the optical transmittance of a scanning laser beam.

Starting with the original thickness of 825 Å, an area of 1.0×2.5 cm^2 is raised above the electrolyte and a thickness of 100 Å is anodized using the same constant current. Next the substrate is raised by one centimeter and another 100 Å is anodized. This procedure is repeated until there are several areas with thicknesses varying from 825 to 200 Å. The step between two different thicknesses is clearly visible due to the distinct color reflected by each thickness under ordinary white light so that films with varying thickness can be cut and separated for electrical and magnetic measurements.

Both the inductive χ' and resistive χ'' components of the ac magnetic susceptibility are measured as a function of temperature utilizing a homebuilt ac susceptometer[17] placed inside a mu-metal cyclindrical container which attenuates the external magnetic fields to less than 1 mOe. A niobium film of approximately 0.5×0.5 cm^2 cross section is cut and placed on the sample holder such that the ac driving magnetic field is perpendicular to the surface of the film. The film is then positioned into one of the secondary coils and the voltages arising from both inductive and resistive components are plotted continuously on an X-Y plotter as the temperature is slowly changed. The ac magnetic field ranges from 41.7 mOe to 4.17 Oe in amplitude and operates at a frequency of 250 Hz. The onset temperature for the appearance of superconductivity is taken as the temperature where the first detectable diamagnetic response could be observed in the inductive signal. Subsequent to these magnetic measurements, the same thin film samples are scribed into an H-shaped pattern for electrical measurements using a standard four-probe technique. The electrical contacts are made by first coating the film surface with Kodak Ortho® photoresist[18] and then soldering gold wire leads onto the surface with indium. This method enables the indium to penetrate through the oxide layer and to secure the leads to the niobium layer. The resistive transitions are typically 0.2 K in width, even for the thinnest films, and the superconducting transition temperature T_c is determined as the midpoint between the temperatures of the 10 and 90% normal-resistance points.

III. RESULTS AND DISCUSSION

The superconducting transition temperature T_c determined from resistive and magnetic measurements are in good agreement with each other and show an approximate linear decrease with respect to the reciprocal of the film thickness d as well as to the sheet resistance R_S as seen in Fig. 1. In comparison to earlier results on thin Nb films,[6–8] the present $T_c(d)$ for similar thicknesses are about 1 K lower, even for the extrapolated T_{c0} at infinite thickness. This T_c decrease suggests that the present Nb films are more disordered. This conjecture is further supported by the larger residual resistivity (normal-state resistivity at 10 K) of approximately 25 $\mu\Omega$ cm (see Fig. 2) as compared to the saturated 18–22 $\mu\Omega$ cm values from earlier work.[8,10] It has been previously established even for bulk films that T_c can be substantially reduced by larger bulk (residual) resistivity values. From T_c vs residual resistivity data for Nb films,[9,10] a 25-$\mu\Omega$-cm resistivity results in a $T_c\approx7.2$ K, in reasonable agreement with the T_c value for our thickest film of 825 Å. Also utilizing the intrinsic value[6] of $\rho_i l_i=3.72\times10^{-6}\mu\Omega$ cm^2, then the mean free path l for the present films would be approximately 13 Å, which is about a factor of 30 times smaller than that for the best crystalline Nb films.[6] Thus

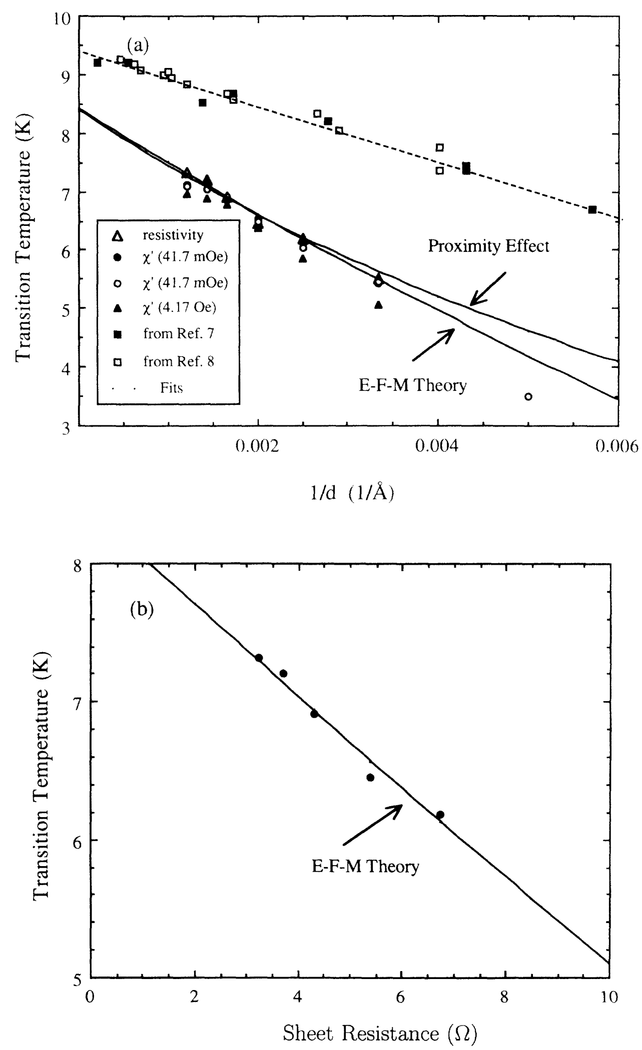

FIG. 1. The superconducting transition temperature T_c from electrical (△) and magnetic (●,○,▲) measurements for anodized Nb films as a function of (a) the thickness d and (b) the sheet resistance R_S. The upper graph indicates the present T_c results are about 1 K below earlier results on Nb films from Refs. 7 and 8. The solid lines are fits of Eq. (1) for the proximity effect and Eq. (2) for the Ebisawa-Fukuyama-Maekawa theory of localization to the present Nb results. The dashed line is to serve as a guide to a linear behavior.

these results support our conjecture that the present Nb films are more disordered and are in the dirty superconductor limit.

One also observes that the suppression of T_c in the present data with decreasing thickness is greater than the earlier results on crystalline Nb films. In order to distinguish the mechanism responsible for this suppression of T_c, one notes that the residual resistivity is fairly constant for thicknesses of 400 Å and greater as shown in Fig. 2. This independence of thickness indicates a saturated resistivity with essentially no change in the normal-state electrical properties or in the bulk chemical composition of the unanodized Nb films. Thus the T_c dependence upon d^{-1} is probably not directly affected by any bulk resistivity effect nor any bulk oxygenation effect due to the anodization process. However, for the films less than 400 Å thick, this may not be the case as structural inhomogeneties and increased grain-boundary scattering may have a significant influence. To further clarify whether the T_c suppression is due to the proximity effect or weak localization effects, an attempt to fit the data to the corresponding equations for these effects was initiated. From the localization model for dirty thin films proposed by Ebisawa, Fukuyama, and Maekawa[19] the suppression of T_c with thickness d is given by equation of the form

$$\ln\left[\frac{T_c}{T_{c0}}\right]=-\left[\frac{e^2R}{2\pi^2 h}\right]f[E_0,\omega_D,\mu^*,g^{-1},\ln\Gamma,\ln b,\ln(hD\kappa^2/2\pi k_B T_c)] , \quad (2)$$

where $E_0=hD(2\pi/d)^2$, $\Gamma=h/2\pi\tau_0 k_B T_c$, $b=E_0/2\pi k_B T_c$, and $\kappa^2=6\pi n_0 e^2/E_F$. T_c and T_{c0} are the superconducting transition temperatures of the film with and without impurity scattering ($d\rightarrow\infty$). D, κ^{-1}, μ^*, and τ_0 are the diffusion constant, the two-dimensional screening length, the renormalized effective Coulomb repulsion, and the elastic-scattering time, respectively. The equation contains corrections due to change in density of states, retardation of the Coulomb interaction, and the enhanced Coulomb interaction. Utilizing standard values for the Fermi energy E_F, the Debye frequency ω_D, and the electron density n_0 for Nb, Eq. (2) is solved numerically with a value of $T_{c0}=8.4$ K. In order to obtain a reasonable fit to the experimental data as seen in Fig. 1, an arbitrary prefactor of 14 is necessary to produce sufficient suppression of T_c. This value is extremely large when compared to the value of unity for the screened Coulomb interaction[20] in the long-wavelength limit. This suggests that localization cannot be the only or even the primary source for the T_c suppression in our Nb films. If one utilizes Eq. (1) which is associated with the proximity effect, a ratio of 60 for $a/N(0)V$ is needed to fit the present data. (See Fig. 1.) For pure Nb, the bulk interaction potential[21] $N(0)V=0.32$ and thus a normal-surface layer of 19 Å is required. Although this normal layer may be considered too large,[22] it is known from work on the effects of interstitial oxygen on Nb films[23] and disordered Nb films[1] that the density of states decreases from the bulk value when disordered is introduced. Thus a factor of 2 decrease in the $N(0)V$ value would result in a similar decrease of the normal-surface layer thickness. Even though the anodization process is creating insulating Nb_2O_5, a metallic surface layer of $NbO_{1\pm x}$ could be formed on the order of 10 Å, i.e., two-to-three atomic layers.[22] Thus the suppression of T_c vs d^{-1} for $d\geq 400$-Å-thick Nb films is probably attributable to both the proximity effect and localization. Since the residual resistivity dramatically increases for films less than 400 Å thick, the T_c suppression is probably a result of increased grain-boundary scattering[24] as the grain size becomes comparable to the film thickness and of increased disorder arising from structural inhomogeneities developing on the length scale of these film thicknesses. As seen in Fig. 1, the T_c for the thinnest film of 200 Å lies below the straight line fit and correspondingly the depression in T_c of this film is due to all three effects: proximity effect, localization, and an increased residual resistivity effect.

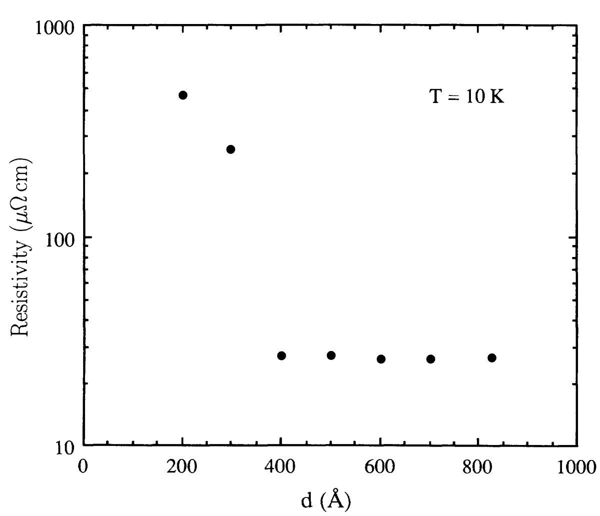

FIG. 2. The residual resistivity is determined from the normal-state resistance measured at 10 K.

The second aspect of this study focuses on the effect of the Nb film thickness upon the magnetic properties. Figures 3 and 4 show the temperature dependence of the inductive χ' and resistive χ'' components of the ac susceptibility for three different ac magnetic fields. Clearly the onset temperature of a diamagnetic response decreases with decreasing film thickness as previously summarized in Fig. 1. However, the onset temperature has only a weak field dependence upon careful inspection of the raw data. Secondly, the width of the transition to a complete flux exclusion[25] (or perfect magnetic shielding) of $\chi_{SI}=-1$ becomes progressively broader with decreasing thickness d as well as with increasing ac field strength. In fact at the largest field amplitude of 4.17 Oe, the χ' data at 4.2 K are significantly smaller than the maximum value of -1 even though some flattening appears at these temperatures. These features in χ' are consistent with the corresponding χ'' data shown in Fig. 4. The χ'' peak structure broadens with increasing field strength and to some extent with decreasing film thickness. Furthermore the χ'' for the 4.17-Oe field remain nonzero to the lowest measured temperatures indicating resistive dissipative processes are still prevalent.

The appearance of a nonzero χ'' signal below T_c is ubiquitous for all bulklike and granular superconductors and arises from the intragranular and/or intergranular coupling between smaller superconducting regions within the sample. Various models[26] have been proposed to explain the χ'' peaks, including average conductivity or eddy-current models and magnetic hysteresis models. In the conductivity models,[27] a rapid change in the effective conductivity below T_c gives rise to an eddy-current-type dissipative process in χ'' which will vanish when infinite

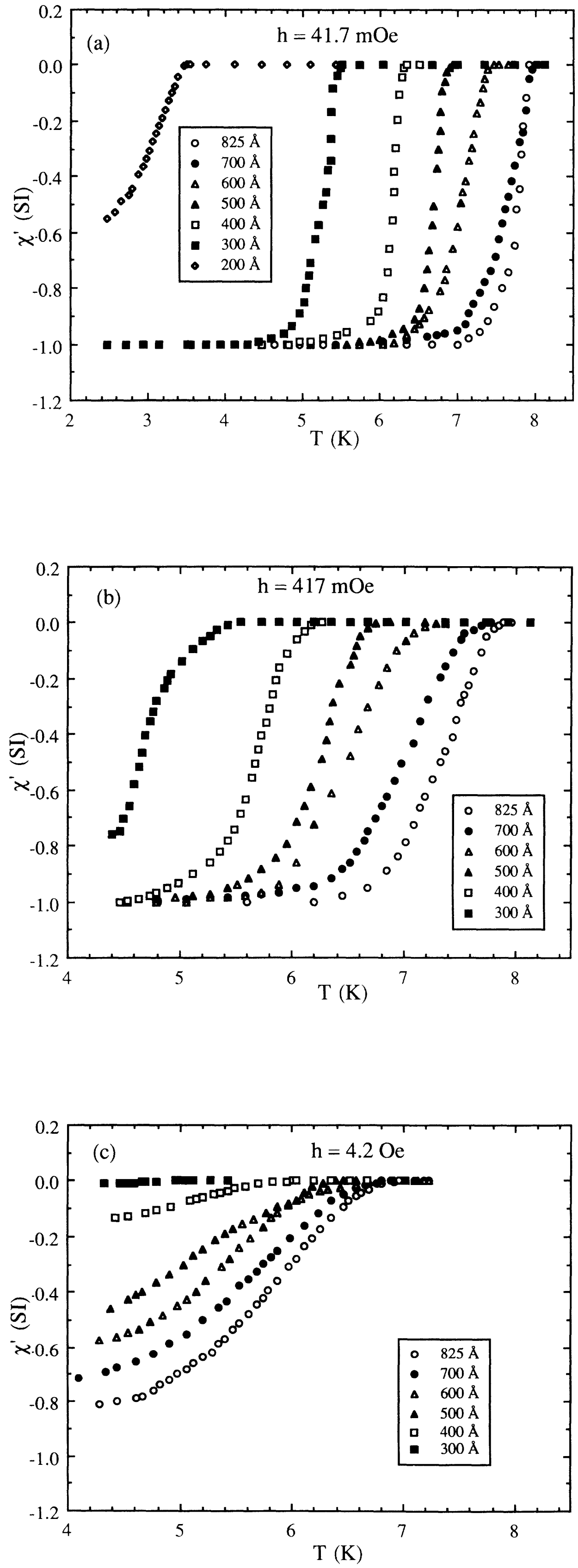

FIG. 3. The inductive component χ' of the ac magnetic susceptibility on the Nb films as a function of temperature for ac fields of (a) 41.7 mOe, (b) 417 mOe, and (c) 4.17 Oe.

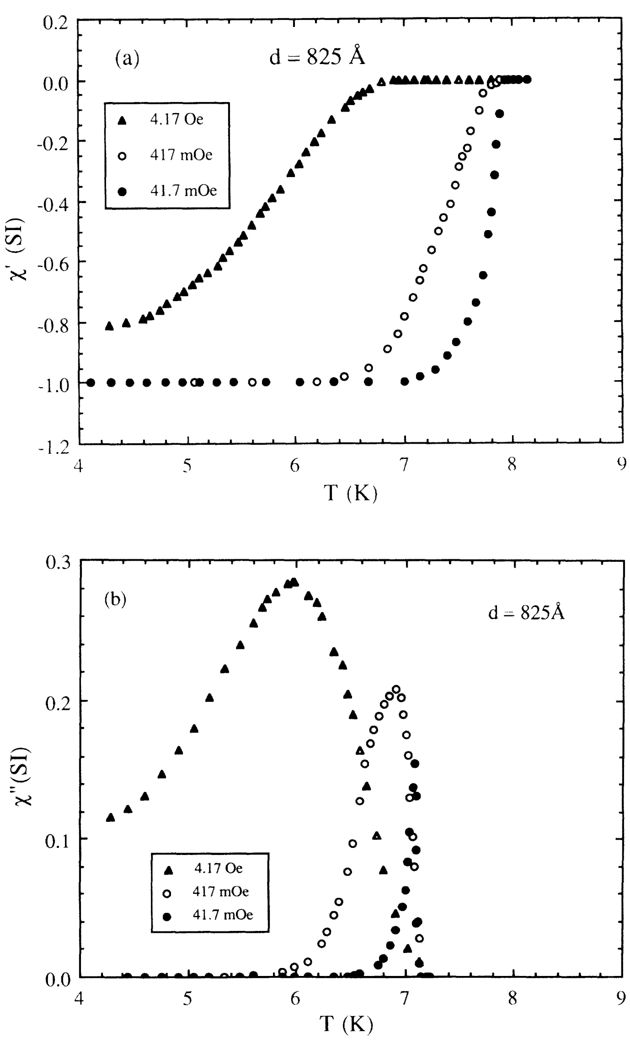

FIG. 4. The (a) inductive χ' and (b) resistive χ'' components of the ac magnetic susceptibility for the 825-Å-thick Nb film versus temperature for different ac magnetic fields.

conductance is realized. The magnetic hysteresis models utilize the idea that irreversible M-H loops develop in type-II superconductors due to flux-trapping phenomenon, since the driving ac field can exceed the lower critical field H_{c1} just below T_c. The χ'' data have been modeled by utilizing critical-state models[28–30] of Kim and Bean as well as considering the flux jumps that can occur in multiple-connected Josephson-junction-type networks.[31,32] In either case of the hysteresis models, the χ'' peaks result from the driving ac field exceeding H_{c1} and the irreversibility in the superconducting materials.

Since χ' (4.17 Oe) is not maximized and χ'' (4.17 Oe) is nonzero at $0.6T_c$ for the 825-Å-thick film, then the internal magnetic field arising from the driving field of 4.17 Oe must exceed the lower critical field. In order to obtain an estimate of this internal field for the geometric configuration of the driving field h_{ac} being perpendicular to the surface of the film, we recall that the demagnetization factor D can be determined from the following expression:

$$\chi'_{\text{measured}}(\text{cgs}) = -\frac{\text{Volume}}{4\pi}\frac{1}{(1-D)} . \quad (3)$$

For the 825-Å-thick film, we find

$$1/(1-D) \approx 2\times 10^4 .$$

Thus the effective critical field H_{c1}(eff) for complete flux exclusion will be reduced to

$$H_{c1}(\text{eff}) \approx H_{c1}(1-D) \approx 0.09 \text{ Oe} , \quad (4)$$

since $H_{c1}(0)$ for bulk Nb is 1735 Oe.[33] Thus driving fields of less than 0.1 Oe must be used to observe complete flux expulsion which is in accordance with the results in Figs. 3 and 4. Thus the broadening of the diamagnetic transitions in χ' and χ'' with larger driving fields would appear to result from the magnetic hysteresis caused by the extremely large internal fields created by the geometric demagnetization factor.

An alternative way to investigate the magnetic properties would be to measure χ' and χ'' with the driving field h_{ac} parallel to the film surface and thus minimize the large demagnetization effect on H_{c1}. However, even for this parallel field-film arrangement, there are other problems dealing with experimental detection to consider. First, the ratio of the (Volume/4π) is a factor of 2 smaller than the sensitivity of our ac susceptometer (2×10^{-7}emu) even for the thickest film of 825 Å. Secondly, the effect of the magnetic-field penetration into the film is a more severe limitation in these measurements. For the 825-Å-thick film, this thickness is approximately equal to twice the intrinsic penetration depth λ_L of 390 Å for pure Nb.[34] Utilizing London's equation and the appropriate boundary conditions for an infinitely long film of thickness d, one can easily show[35] the diamagnetic response is suppressed to about 10% of the maximum value of (Volume/4π) when $d \approx 2\lambda_L$. This suppression of the diamagnetic response can be further enhanced by another order of magnitude since the penetration depth for a dirty superconductor is increased as $\lambda \sim \lambda_L(\xi_0/l)^{1/2}$, which results in $\lambda \approx 2100$ Å for mean-free-path estimates of 13 Å in the present films. Thus within the present experiment magnetic measurement capabilities, one cannot measure a diamagnetic response for Nb films less than several thousand Å thick. Thus there are two inherent problems in experimentally detecting a diamagnetic response (flux exclusion) in small, two-dimensional-like regions of superconducting materials, even if they are continuous and homogeneous as in the present investigation of these Nb films.

In conclusion, the suppression of T_c in a Nb film as a function of thickness through an anodization process has been measured. The suppression appears to be explained by a combination of the proximity effect and weak localization for thicknesses of 400 Å and greater. For thinner films, the bulk resistivity effect also contributes to the T_c suppression. The magnetic measurements show as a function of increasing magnetic field and decreasing thickness that the superconducting transition becomes progressively broader and the flux exclusion becomes smaller. These features point out the experimental difficulty in measuring diamagnetic responses from two-dimensional-like superconducting regions or samples.

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