Superconducting Proximity Effect of Nb†

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Previous investigators have studied the proximity effect of a number of nontransition-metal superconductors. In this investigation the proximity effect of Nb (a transition-metal superconductor) has been studied using the Nb–Cu and Nb–Ni systems. The films were sputtered sequentially without breaking vacuum. The sandwiches were maintained at temperatures below 200°K until after T_c had been measured, to preclude chemical or metallurgical interactions. Sandwich T_c has been obtained as a function of Nb film thickness for thick overlayer films. The Nb–Cu data are in agreement with the de Gennes-Werthamer theory. The Nb–Ni data follow the form of the adjustable-parameter $(\beta\equiv\hbar/2\pi k_B\tau_s)$ theory proposed by Werthamer. However, Ni is found to have less effect on Nb than was reported for Pb: a value of $\beta=7$ is obtained for Nb compared to $\beta=43$ for Pb. Possible explanations of the observed behavior are discussed.

I. INTRODUCTION

THE proximity effect of a superconductor (SC) in contact with a normal metal (N) has been studied experimentally in a number of previous investigations.[1–6] There are also a number of theories based in the microscopic theory of superconductivity which have been proposed to explain the proximity effect.[7–11] Only the de Gennes-Werthamer theory[8] and an extension of it by Moormann[11] provide closed-form solutions and involve no adjustable parameter with which to fit data. Both have been shown to correlate well with the more recent experimental results in which precautions have been taken to preclude the possibility of chemical and metallurgical interactions at the interface between the two metals.[5,6] Most of these experiments used Pb as the SC; to date no results have been reported in which a transition-metal SC was used.

The proximity effect of a magnetic metal (Mag) and a SC has also been studied[1,4,5,12,13]—again, only in detail with Pb as the superconductor. Theoretically the SC-Mag system is not as well understood as the SC-N. For dilute concentrations of magnetic impurities in a superconductor, Werthamer[12] has combined the Abrikosov-Gor'kov theory with the proximity-effect theory. The magnetic character of the impurities enters only through a parameter τ_s, a "lifetime" for a superconducting pair in a spin scattering environment. When applied to a SC-Mag system, in which there are large concentrations of magnetic "impurities," τ_s becomes an adjustable parameter, and the theory must be considered to be quasiphenomenological. Experiments on SC-Mag sandwiches[12] show that the form of the theory does roughly fit the data. The magnitude of $1/\tau_s$ is found to increase as the magnetic strength of the overlayer film increases. However, the question which now must be answered is whether τ_s is specified only by the magnetic nature of the material. This question may be tested by using other superconductors to see if the same value of τ_s will match the theory to the experiments. Transition-metal superconductors (TMSC) are particularly attractive for this experiment since TMSC-Mag systems are expected to be more sensitive to variations in τ_s, a consequence of their higher density of states near the Fermi level. TMSC-Mag are also interesting in light of Matthias's provocative (albeit, not too widely accepted) suggestion that the superconductive ordering in the transition-metal SC's may be due to a magnetic interaction.[14]

In this investigation the proximity effect of Nb (TMSC) is studied with Cu (N) and Ni (Mag). The Nb film thickness is varied for a thick overlayer film, and the sandwich T_c is measured. The results reported here are divided into three parts. The Nb films themselves are characterized first since some of their important properties vary with thickness in the range of interest. The Nb–Cu system is then examined to verify the applicability of the theory to Nb. Finally the Nb–Ni system is studied. The results obtained are compared with theory and with the experimental results reported for nontransition-metal superconductors.

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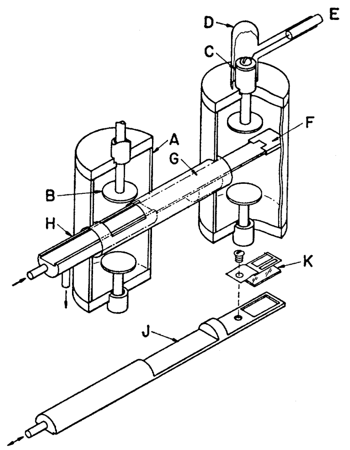

FIG. 1. Sputtering apparatus. A, anode can; B, cathode (1in. diam); C, quartz insulator; D, pyrex shield; E, high voltage; F, presputtering shield; G, 0.010 in. ss strip inside tube; H, liquid-N_2 filled Cu block; J, substrate transport; K, substrate.

II. EXPERIMENTAL

A. Procedure

The films in the proximity-effect sandwiches are deposited by sputtering in the apparatus shown in Fig. 1. It is similar to one described earlier by Hauser.[12] One film is deposited after the other without breaking vacuum. Polished 100 faces of MgO single crystals are used as substrates. The substrate is masked so that two separate deposits are obtained: a 4×12-mm sandwich of Nb/overlayer and a 2×12-mm film of the overlayer alone. The electrode materials are 99.97% or greater purity. The sputtering is carried out in 0.99999% pure tank argon. The argon is admitted to the belljar after the liquid-N_2 trapped, mercury diffusion-pumped system is evacuated to its ultimate vacuum (1.5×10^{-6} Torr). The electrodes are then presputtered for a period of 1 h. During this period the substrate is under a shield in the Nb sputtering chamber where it receives an in-vacuum heat cleaning. The Nb films are deposited without bias at a pressure of 50 μ, dc cathode potential of 4 kV, and discharge current of 10 mA. Under these conditions the substrate temperature is approximately 350°C and a deposition rate of 600 Å/min is obtained. The anode can is cooled to 115°C during deposition by a controlled flow of cold N_2 gas through cooling coils in contact with the can exterior. Before the overlayer films are deposited the substrate is positioned under pressure-contact directly on a liquid-N_2 filled copper block. A delay of 5 min is required for the substrate temperature to reach equilibrium. The substrate temperature is thus maintained well below 200°K during the deposition of the overlayer film, preventing the occurrence of atomic diffusion or chemical interaction between the two metals. The Ni and Cu films are typically deposited at a pressure of 35 μ, cathode potential of 2 kV, discharge current of 1–2 mA, and anode can temperature of ~250°K. The deposition rate for Cu is ~100 Å/min; for Ni, 60 Å/min. After sandwich formation the vacuum system is backfilled with dry nitrogen gas and the substrate is dropped into a container of liquid nitrogen. This process takes 1–2 min during which time the substrate temperature remains below 200°K. The sandwich is now mounted under liquid nitrogen into a sample holder equipped with pressure contacts for four terminal resistance measurement. The holder is in turn inserted into a precooled cryostat. After the critical temperature is measured, the sandwich is warmed to room temperature in a desiccator while the resistance of both the sandwich and overlayer films are monitored to obtain room-temperature/10°K resistance ratios. Because Nb is not attacked by dilute nitric acid in which both Ni and Cu are readily etched, the overlayer film can be removed, permitting data on the Nb film actually used in a particular sandwich to be obtained. There is no significant change in the T_c or thickness of bare Nb films exposed to the identical processing received by sandwiches.

B. Measurements

The sputtering pressure measurements are made with an air-calibrated NRC thermocouple gauge. In practice, the discharge impedance was found to be much more sensitive to pressure variations than the gauge. Consequently, it was used to obtain reproducible pressures. The sandwich transition temperatures were obtained by monitoring their resistance with a four-terminal pressure-contact method. Measuring currents were typically 10 μA. A Honeywell Ge resistance thermometer

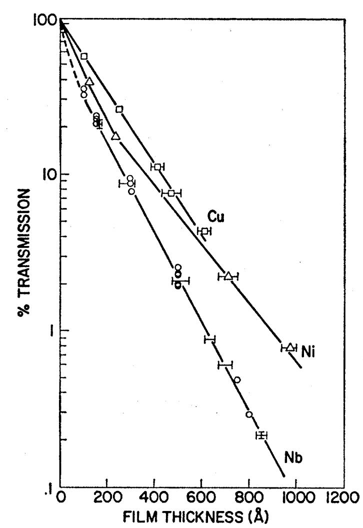

FIG. 2. Tolansky calibration of percent transmission versus film thickness for Nb, Cu, and Ni films deposited under sandwich deposition conditions.

was used as a temperature sensor. Its resistance was determined with a Leeds and Northrup K-3 potentiometer. Thickness measurements were made with a light-transmission technique, using a frosted incandescent lightbulb for a light source. The variation of the percentage transmittance with thickness was calibrated using the Tolansky technique for thicker films (Fig. 2). Shorter deposition times with known deposition rates were then used to obtain values of percent-transmittance for the thinner films. Resistivity values were obtained from four-point probe resistance measurements. The apparatus and techniques used are described in greater detail elsewhere.[15]

III. RESULTS

A. Nb Films

It has been reported by a number of previous investigators[16–19] that the T_c of films of transition-metal superconductors is lower for films less than several thousand angstroms. The consensus is that this falloff of T_c is caused by structural effects rather than substrate contamination. The introduction of impurities *is* known to decrease the T_c of bulk Nb.[20] But even in this case the effect on T_c is attributable to the distortion of the lattice caused by the impurities.[21] Further suggestion of the dependence of T_c on film structure has been found in the course of this investigation. Table I(a)

TABLE I(a). Effect of substrate material on 500 Å Nb films. (b). Comparison of thick Nb film with electrode material. (c). Effect on 500 Å Nb film of cooling substrate after deposition.

	Experimental conditions	T_c	$\rho_{300\,°K}/\rho_{10\,°K}$
(a)	Soda lime	8.70	3.4
	Pyrex	8.60	3.1
	Quartz (polished)	8.80	3.3
	Sapphire (polished)		3.4
	LiF (cleaved)		3.4
	MgO (cleaved)	9.10	6.0
	MgO (polished)	9.09	5.8
(b)	10 000 Å film	9.54	6.3
	Electrode material	9.39	24.8
(c)	15 min anneal at 300°C	9.09	5.8
	Quench on Cu at 77°K	9.03	5.3

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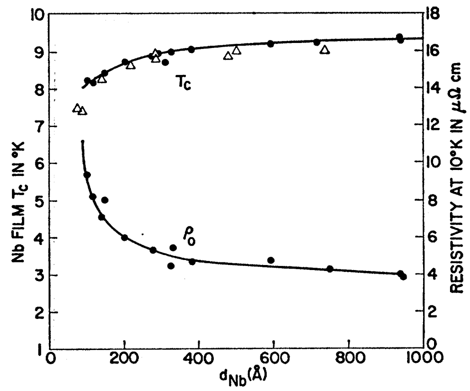

FIG. 3. Nb film transition temperature and residual resistivity versus film thickness.

shows the T_c and $\rho_{300°K}/\rho_{10°K}$ of several 500-Å films which were deposited under the same conditions on different substrate materials. The higher T_c and lower resistivity of the films on MgO correlate with Hauser's finding that Nb films deposited on MgO are preferentially oriented.[19] The lower T_c and higher resistivities of the films deposited on other substrates suggest that in these cases the ordering has not taken place.

To take advantage of the ordering which takes place on MgO, this material was chosen as the substrate for the proximity-effect experiments. Little difference was observed in the properties of Nb films deposited on polished 100 MgO surfaces relative to those deposited on cleaved surfaces. Consequently, polished surfaces were used.[22] In this way a more reproducible substrate surface was obtained (cleavage steps were eliminated) and the substrates could be used several times. Even on MgO substrates, however, the properties of the Nb films are not independent of thickness. T_c and low-temperature resistivity variations are shown in Fig. 3. These data were obtained from both Nb films which were actually used in sandwiches (after etching away the overlayer) and from films deposited under the same conditions as the sandwiches, i.e., at a substrate temperature of 350°C followed immediately by quenching on a liquid-N_2 cooled Cu block. The data represented by triangles were obtained in an earlier version of the sputtering system which had an opening in the Nb anode can to admit a thermocouple.

Table I(b) lists the critical temperature and resistivity ratio of a thick Nb film, and those of the bulk material used for the sputtering electrodes. Table I(c) shows the effect of cooling the substrate immediately after deposition, as done in the sandwich depositions.

B. Nb–Cu Sandwiches

The de Gennes-Werthamer theory[6] will be used to compare with the experimental results. The theory is

[22] The final polishing was performed with Linde "B" Al_2O_3 powder mixed with distilled water.

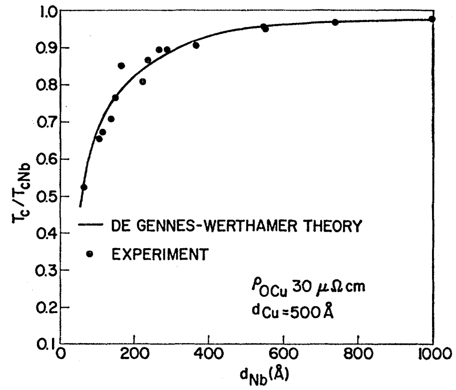

FIG. 4. Nb–Cu sandwich reduced transition temperature versus Nb thickness.

valid in the dirty limit ($\xi_0 \gg l$, electron mean free path). This condition holds for Nb films for which estimates of these quantities are 500 Å and 30–50 Å, respectively.[19] The equations which relate the sandwich T_c to the properties of the films in the sandwich are given below:

$$\chi(\xi_s^2 k_s^2) = \ln(T_{cs}/T_c), \tag{1}$$

$$\chi(-\xi_n^2 k_n^2) = \ln(T_{cn}/T_c), \tag{2}$$

$$[N\xi^2 k \tan kd]_s = [N\xi^2 k \tanh kd]_n, \tag{3}$$

$$\xi_x^2 \equiv \pi\hbar k_B / 6T_c e^2 \gamma_x \rho_x, \tag{4}$$

$$\chi(x) = \psi(\tfrac{1}{2}+\tfrac{1}{2}z) - \psi(\tfrac{1}{2}). \tag{5}$$

ψ is the digamma function[23]; T_{cs}, T_{cn}, and T_c are the critical temperatures of the superconductor, normal metal, and sandwich, respectively; d_s and d_n the superconductor and normal metal thicknesses; ξ is the effective coherence length, defined by Eq. (4); ρ is the electrical resistivity at 10°K; γ is the coefficient of electronic specific heat. N, the density of states at the Fermi level, is assumed to be directly proportional to γ. Thus γ can be substituted for N in Eq. (3). The values of γ used (in erg/cm³ °K²) are Cu, 1.01×10^3 [24]; Nb, 6.95×10^3.[25] Since the theory is insensitive to the value of T_{cn} when $T_c \gg T_{cn}$, $T_{cn}=0$ has been used.

The Nb–Cu sandwiches of various Nb film thicknesses were made with 500 Å Cu films. At this thickness, for the values of $\rho_{0\,\mathrm{Cu}}$ obtained, T_c is no longer sensitive to variations in d_n. In each case the values of the other parameters used were those measured for the films comprising a particular sandwich. Since substrate temperature (and hence resistivity) control is difficult for the overlayer film in experiments of this nature, this method is necessary. For most of the sandwiches made, the Cu resistivity was between 20 and 40 μΩ cm, but values of 10 and 60 μΩ cm were also obtained.

The value of ρ_0 used is in all cases the thickness average value. That is, variations in electron mean free path l due to structural variations within the film are ignored. The theory assumes that l is uniform throughout a film even though it is known to vary. This failure of the experiments to meet an assumption of the theory is believed to constitute the largest source of error in the data-theory comparison. The effect of the error is mitigated to some extent because resistivity enters the theory as $\rho_0^{1/2}$.

The data and the theory compare favorably for each sandwich. Therefore the theory has been used to adjust the value of d_{Nb} to that corresponding to a Cu layer of $\rho_{10°\mathrm{K}}=30$ μΩ cm. Disparity between theory and experiment has been preserved in this procedure. Thus adjusted, the data are plotted in Fig. 4. The T_c's obtained were in each case but one within 5% of the value predicted by the theory. This agreement is considered good in light of the difficulty in controlling resistivity. It is taken as evidence that the theory is applicable to Nb and that no barrier of any consequence accumulates between the films in the period between their deposition allowed for substrate cooling.

The Moormann theory (in the dirty limit) was also applied to the results using a value of $\Theta_{\mathrm{Nb}}=238°\mathrm{K}$ [25] and $T_{c\,\mathrm{Cu}}=0.07°\mathrm{K}$.[5] The calculated T_c's agree to within 0.1°K with the result obtained from the de Gennes-Werthamer theory.

C. Nb–Ni Sandwiches

In the absence of any theory for the superconducting behavior of a SC-Mag sandwich, Werthamer[12] has attempted to obtain an approximate description by adapting the theory of Abrikosov and Gor'kov for dilute

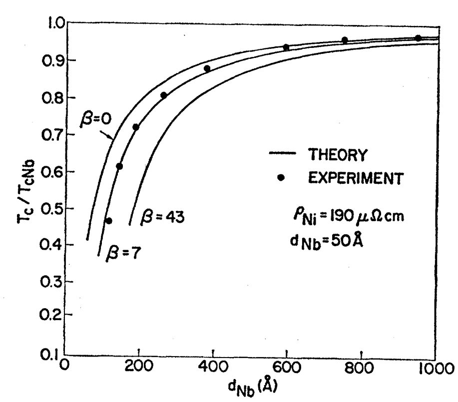

FIG. 5. Nb–Ni sandwich reduced transition temperature versus Nb thickness.

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concentrations of randomly oriented paramagnetic impurities in a SC. The effect on the theory of replacing a normal metal overlayer with a magnetic one is to add an additional term to the argument of the χ function in Eq. (2) with the result

$$\ln(T_{cn}/T_c)=\chi[-\xi_n^2k_n^2+(\hbar/2\pi\tau_s k_B T_c)], \quad (6)$$

where τ_s is an unknown "lifetime" of superconducting pairs in the spin-scattering environment of the magnetic material. If τ_s and the constants are lumped into $\beta\equiv(\hbar/2\pi\tau_s k_B)$, Eq. (6) becomes

$$\ln(T_{cn}/T_c)=\chi(-\xi_n^2k_n^2+\beta/T_c). \quad (7)$$

Equation (7) is used to replace Eq. (2). Equations (1), (3)–(5), and (7) then provide a solution for the critical temperature of a SC-Mag sandwich. A value of β is obtained by fitting the theory to the experimental data.

The sandwiches were made with 50 Å of Ni. Because of the effectiveness of the spin scattering, this thickness has the same effect on T_c as thicker Ni layers. The scatter in the Ni resistivity was somewhat smaller than obtained for Cu, all but two films having resistivities between 150–200 $\mu\Omega$ cm.

In applying the theory, $T_{cn}=0$ and $\gamma_{\mathrm{Ni}}=10.8\times10^3$ ergs/cm^3 °K^2 [24] were used. Each sandwich was individually compared with the theory to obtain a value of β. There was no apparent dependence of β on $\rho_{0\,\mathrm{Ni}}$. This value of β was then used with the theory to correct the data to $\rho_{0\,\mathrm{Ni}}=190$ $\mu\Omega$ cm and the results plotted in Fig. 5. Superimposed on the data are theoretical curves corresponding to several values of β. The $\beta=0$ curve corresponds to the assumption that the magnetic nature of Ni has no effect (or that Ni is a normal metal). The $\beta=43$ curve is shown because this is the value that Hauser found for the Pb–Ni system with 190 $\mu\Omega$ cm Ni overlayers. The data obtained in this investigation are best fitted by using $\beta=7$. That is, the Nb films appear to be less affected by the presence of the Ni overlayer than are the Pb.

IV. DISCUSSION

The reason for the smaller proximity effect observed in the Nb–Ni sandwiches is not understood. Several factors which could cause the observed behavior are discussed below. The possibility of a thin barrier between the films, or of an interaction at their interface can not be ruled out. However, the precautions taken, the data on the Nb–Cu sandwiches and the experience of other investigators suggest that it is at least on a small enough scale to be unimportant.

It is also possible that the value of β may be influenced by other factors than the magnetic nature of the material. For example, the structure of a Ni film on Nb may be quite different from one on Pb. Critical temperature changes of >1°K resulting from such structural effects have been observed in Pb–Cu [26] and Pb–Pt [6] proximity effect experiments. Reversing the order of deposition of the films, thereby changing the structure of the Cu or Pt atom layers adjoining the Pb, results in the changed T_c. This effect would be more pronounced in the case of a Ni overlayer where the region of the Ni film affected by the Nb surface $\simeq\xi_n$. Unfortunately, the requirement that Nb be deposited on a hot substrate precluded the possibility of reversing the order of deposition in this work. To determine whether the $\rho_{0\,\mathrm{Ni}}$ is significantly influenced by the Nb film, 50 Å of Ni was simultaneously deposited on MgO directly and on $\sim$15 Å Nb on MgO. Even though Ni fills in spaces between Nb islands, thereby giving the Nb a larger conductivity than would be expected, it could be concluded that the presence of Nb on the substrate did not substantially increase $\rho_{0\,\mathrm{Ni}}$.

Finally, it is possible that Nb is different from Pb in some way relevant to the observed results. The fact that Nb is a transition-metal SC may be important. Also, magnetic impurities in Nb are known to lose their localized moment.[27] This suggests the possibility that a neutralization of some of the spin scattering centers adjacent to the Nb–Ni boundary may be taking place, perhaps due to some interpenetration of Nb and Ni.

The difficulty in understanding the behavior of the SC-Mag system is that the sandwich T_c is completely controlled by the first 2–4 atom layers of Ni adjoining the Nb. The condition of this Ni is unknown and controlled to a large extent by the surface on which it is deposited. Therefore any quantitative comparison of experimental results on SC-Mag sandwiches or experimental evaluation of theoretical advances will require a much more detailed knowledge of the condition of the interface between the two metals.

ACKNOWLEDGMENT

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