Oscillatory Superconducting Transition Temperature in Nb/Gd Multilayers

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The superconducting transition temperature T_c in Nb/Gd multilayers shows a pronounced nonmonotonic dependence on the ferromagnetic Gd layer thickness d_{Gd} for fixed Nb thickness d_{Nb}. For $d_{\mathrm{Nb}} = 500$ and 600 Å, the T_c oscillation occurs in the range $10 \leq d_{\mathrm{Gd}} \leq 40$ Å where the Gd ferromagnetism is well established. These results provide the first evidence for the predicted π phase in superconductor/ferromagnet multilayers where the order parameter in neighboring superconducting layers may have an intrinsic phase difference.

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In certain situations the Josephson coupling between two superconductors may lead to a junction with an intrinsic nonzero phase difference. It was originally proposed by Bulaevskii, Kuzii, and Sobyanin that an intrinsic phase difference $\Delta\phi = \pi$ is possible if magnetic impurities are present in the tunnel barrier [1]. One manifestation of this effect would be a ground state with a spontaneous persistent current in zero applied magnetic field in a ring containing such a junction. It has recently been suggested that these so-called π junctions may also arise in weak links made from superconductors with d-wave pairing [2], and this has led to a number of experiments on high-T_c junctions probing this possibility [3–7]. In light of the current interest surrounding this issue, it is important to determine whether π junctions may exist in other systems.

For the case considered by Bulaevskii, Kuzii, and Sobyanin, coherent tunneling is assisted by a spin-flip process. It has been argued, however, that the impurity density required to give $\Delta\phi = \pi$ is large enough that the impurities are no longer independent, and their interaction will inhibit the spin-flip process [2]. The case of interacting spins in the barrier was considered by Buzdin, Kupriyanov, and Vujicis [8] and Radović *et al.* [9] who predicted the existence of a π phase in multilayers composed of alternating superconducting (S) and ferromagnetic (F) layers. All dynamical spin processes are neglected in their model, the F layers are treated within a proximity effect theory, and the main magnetic influence on the superconductivity is through the exchange field I in the magnetic layers. By solving the Usadel equations for the dirty limit they found that the Cooper pair wave function in the ferromagnetic layers exhibits damped oscillatory behavior with a characteristic length scale $\xi_M = \sqrt{4\hbar D_M/I}$, where D_M is the diffusion constant in the ferromagnetic layer. The local exchange field in the ferromagnetic layers produces a phase shift in the superconducting wave function as the Cooper pairs diffuse through the F layers [9]. For certain magnetic layer thicknesses d_F, a state with $\Delta\phi = \pi$ between neighboring superconducting layers was found to have a higher T_c than the ordinary state with $\Delta\phi = 0$. Consequently, superimposed on the suppression of T_c usually found in superconductor/ferromagnet structures [10–12] there will be oscillations in T_c with d_F as the ground state switches between these two phases.

To date there has been no unambiguous experimental observation of this predicted T_c oscillation. It has been suggested [9] that experiments on V/Fe multilayers [13] show evidence for an oscillatory T_c, but a more detailed study on the same system did not observe such an effect [14]. Recently Strunk *et al.* reported measurements on Nb/Gd/Nb triple layers [15]. No T_c oscillations were found, but steplike features in T_c vs Gd thickness d_{Gd} were observed. These were attributed to an enhancement in the pair-breaking mechanism due to the onset of ferromagnetism in the Gd films. In this Letter, we present the results of a systematic study of the superconducting transition in Nb/Gd multilayers. We have observed clear nonmonotonic behavior of T_c as d_{Gd} is varied for fixed Nb thickness d_{Nb}. These results provide the first evidence for a nontrivial superconducting ground state in a multilayer system.

Niobium and the rare earths are immiscible, and very clean Nb/rare-earth multilayers with sharp interfaces can be grown. We prepared Nb/Gd multilayer samples on room temperature Si(100) substrates by dual-source dc magnetron sputtering using 99.9995% pure argon gas at 4 mTorr pressure. The sputtering chamber was evacuated to 10^{-8} Torr before deposition using solid Nb (99.8% pure) and Gd (99.9% pure) targets at rates of 2.5 and 0.4–1.6 Å/sec, respectively. Layer thicknesses were controlled during growth with quartz-crystal monitors and later verified with a profilometer. The measured thicknesses were corroborated by low-angle x-ray diffraction. In all cases, the agreement is within 5%. Despite this, samples grown in separate sputtering runs show enough scatter in T_c to hinder unambiguous observation of nonmonotonic behavior as d_{Gd} is varied. To make a careful study of the dependence of T_c on d_{Gd} it is essential that the samples be deposited under identical conditions. To this end we grew multilayers with wedge-shaped Gd layers

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and uniform Nb layers. The Gd thickness could be varied by a factor of 4 across the wedge. These films were cut into strips perpendicular to the wedge, giving a series of samples with identical d_{Nb} but different d_{Gd}. The strips were ~2 mm wide, which gave a variation of d_{Gd} of approximately 1 Å for each strip. Only every other strip was measured to ensure that the Gd thickness of each sample was distinct. Because all samples in a series are deposited simultaneously, the variation in material parameters is minimized. The multilayers are composed as follows: $Si/Nb_{30\,\text{Å}}/(Gd_{d_{Gd}}/Nb_{d_{Nb}})_N/Gd_{d_{Gd}}/Nb_{30\,\text{Å}}$, where N is the number of repetitions of the Gd/Nb unit and the subscripts denote the layer thicknesses. In the individually grown films $N = 14$; in the wedge films $N = 5$. The top and bottom 30 Å Nb cap layers protect the Gd layers from substrate reaction and oxidation. As will become evident below, superconductivity is suppressed in layers this thin.

Figure 1 shows the low-angle x-ray diffraction patterns of four individually grown films with $d_{Gd} = 25$ Å but with different d_{Nb}. With increasing modulation wavelength, the low-angle Bragg peaks become more closely spaced. The large number of diffraction peaks observed indicates good layering quality. The relative intensity and position of the low-angle diffraction peaks calculated assuming sharp interfaces and the designed layer thicknesses agree well with the actual spectra. Although high-angle x-ray diffraction cannot be used to probe the multilayer quality for the thick layers relevant for this work, high-angle and low-angle data agree well for a similarly grown $(Nb_{58\,\text{Å}}/Gd_{28\,\text{Å}})_{39}$ sample and indicate that the interface roughness is at most 1–2 atomic layers [16].

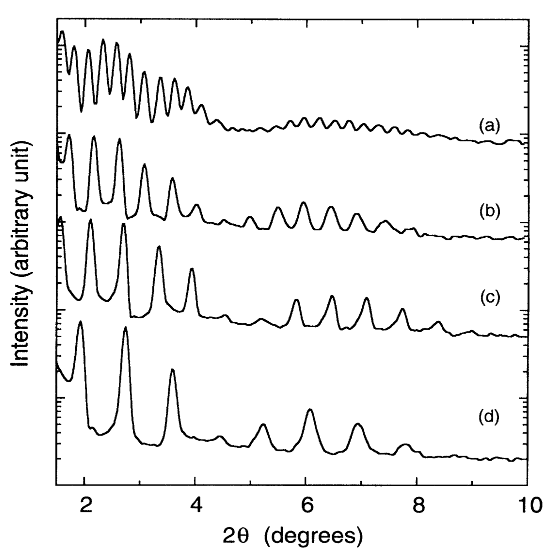

FIG. 1. Low-angle x-ray diffraction spectra of $(Nb_{d_{Nb}}/Gd_{d_{Gd}})_{14}$ multilayers with $d_{Gd} = 25$ Å and (a) $d_{Nb} = 319$ Å, (b) 161 Å, (c) 116 Å, and (d) 81 Å.

To verify that the Gd layers are ferromagnetic, the magnetization $M(T)$ of the multilayers was studied using a SQUID magnetometer in a external field $H = 100$ Oe. The ferromagnetic ordering temperatures T_{Curie} were determined from the inflection points of the $M(T)$ curves. The existence of ferromagnetism was verified by measuring magnetic hysteresis loops at low temperatures. In Fig. 2, T_{Curie} is plotted against d_{Gd} for two series of samples with $d_{Nb} = 400$ and 500 Å. T_{Curie} is depressed from near its bulk value, 292 K, with decreasing d_{Gd} due to finite-size effects [17,18]. Note that for $d_{Gd} \geq 12$ Å, $T_{Curie} \geq 30$ K, and hence the nonmonotonic T_c dependence described below occurs in a d_{Gd} range where ferromagnetic order in the Gd is well established.

The superconducting transitions were measured resistively using a standard four-probe technique. To confirm bulk superconductivity, the Meissner effect was measured by ac susceptibility or dc magnetometry in half of the samples. The magnetic field was applied in the plane of the films. Figure 3 shows the resistance $R(T)$ and ac susceptibility $\chi(T)$ of five samples with $d_{Nb} = 500$ Å but with different d_{Gd} cut from the same wedge-grown film. The resistances are normalized to the residual normal state values R_0 just above T_c, and the susceptibilities are normalized to their asymptotic values χ_0 in the superconducting state. With increasing d_{Gd}, the normal state residual resistivity ρ_0 decreases monotonically from $\simeq 8.5$ to $\simeq 5\ \mu\Omega$ cm. These data show clearly the nonmonotonic dependence of the superconducting transition on d_{Gd}. As d_{Gd} is increased form 5.5 to 12.8 Å, T_c shifts toward lower temperatures. For larger d_{Gd}, however, the trend is reversed, and T_c *increases* as d_{Gd} increases to 18.5 Å. The Meissner effect shows a sharp transition in all samples measured, but the onset of the resistive transition is sometimes broadened, presumably due to small inhomogeneities in the films or damage at the edges produced when the samples were cut. A small feature

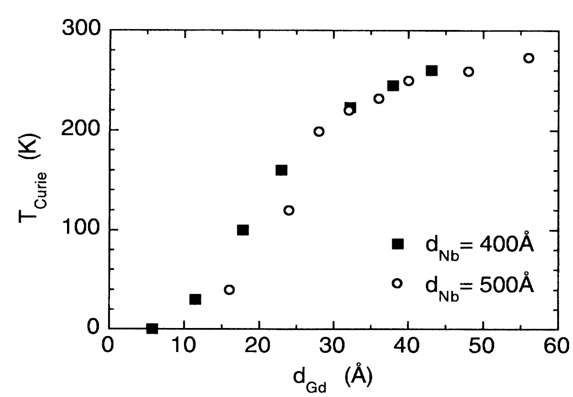

FIG. 2. Ferromagnetic ordering temperature T_{Curie} vs Gd layer thickness d_{Gd} for two series of Nb/Gd multilayers with $d_{Nb} = 400$ and 500 Å.

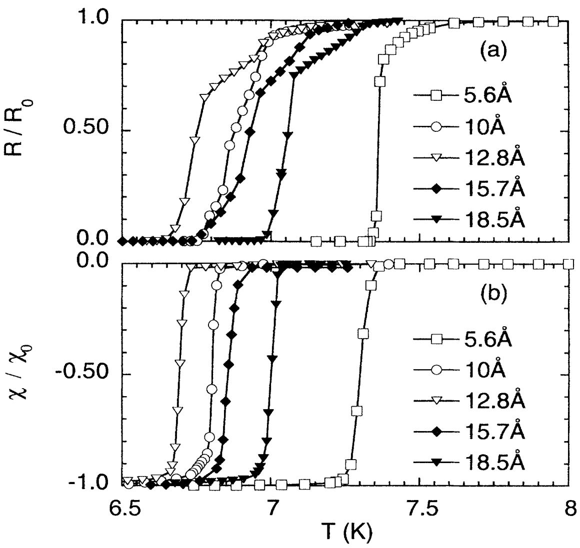

FIG. 3. (a) Normalized resistance R/R_0 and (b) susceptibility χ/χ_0 in Nb/Gd multilayers with $d_{\rm Nb} = 500$ Å and $d_{\rm Gd} = 5.6$, 10, 12.8, 15.7, and 18.5 Å. Normalizations as described in text.

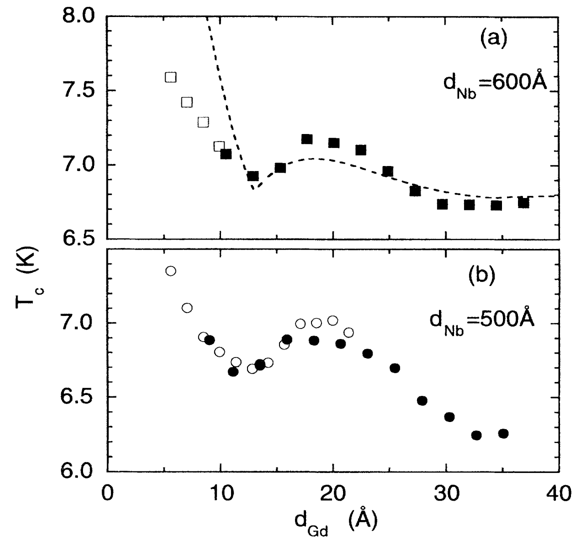

FIG. 4. Superconducting transition temperatures T_c vs $d_{\rm Gd}$ in Nb/Gd multilayers with (a) $d_{\rm Nb} = 600$ Å and (b) 500 Å. Different symbols correspond to different sample series. Dashed line in (a) is a fit by the theory of Ref. [9]. A sputtered Nb film 0.5 μm thick has $T_c = 8.8$ K.

in the susceptibility was observed at the temperature when $R(T)$ begins to drop. In all cases, however, it was less than 1% of the full Meissner signal, and therefore the volume fraction of any damaged or inhomogeneous regions must be less than 0.01 [19]. In all samples where both susceptibility and resistivity were measured, T_c determined from the susceptibility coincides with the point where $R(T) = 0.1R_0$. In those samples where only $R(T)$ was measured, this 10% criterion was therefore used to determine T_c.

Samples covering a wide range of $d_{\rm Nb}$ were measured to determine the best region to observe the oscillation of T_c. As $d_{\rm Nb}$ is reduced below 500 Å, T_c begins to drop rapidly. At $d_{\rm Nb} = 200$ Å, all samples with $d_{\rm Gd} > 10$ Å were found to remain nonsuperconducting down to $T =$ 50 mK. To see superconductivity in samples with thicker Gd layers it was necessary to increase $d_{\rm Nb}$ to at least 350 Å. The effect of $d_{\rm Nb}$ on T_c in Nb/Gd/Nb trilayers has been studied in some detail. Our data for $T_c(d_{\rm Nb})$ are consistent with these results if, as was suggested, $d_{\rm Nb}$ is rescaled by a factor of 2 in comparing multilayer and trilayer data [15]. This is due to the enhanced effect of the magnetic layers on the superconductivity in the multilayer geometry. In a multilayer a Nb layer is coupled to two magnetic layers, while in a trilayer it is coupled to only one.

In Fig. 4 we plot T_c against $d_{\rm Gd}$ for four series of wedge-grown multilayers, two with $d_{\rm Nb} = 600$ Å and two with $d_{\rm Nb} = 500$ Å. A sputtered Nb single film 0.5 μm thick (not shown) has a T_c of 8.8 K, which we take as our bulk value T_{cs}. For both Nb thicknesses, T_c exhibits a rapid drop with increasing $d_{\rm Gd}$, reaching a minimum at $d_{\rm Gd} \simeq 13$ Å. As $d_{\rm Gd}$ is further increased, T_c rises to a maximum at $d_{\rm Gd} \simeq 20$ Å, before decreasing and leveling off at large $d_{\rm Gd}$. For $d_{\rm Gd} \gg 40$ Å, T_c is essentially independent of $d_{\rm Gd}$. For $d_{\rm Nb} = 500$ Å, this asymptotic value is $\simeq 6.1$ K.

For $d_{\rm Nb} = 500$ Å [Fig. 4(b)], the two series covered $d_{\rm Gd} = 6$–24 and 9–36 Å. Although reasonable overlap in the T_c vs $d_{\rm Gd}$ curves are obtained, there are some small differences in the values of T_c for samples with the same nominal thicknesses. Using the value for the mean free path l as determined from the residual resistivity, the superconducting coherence length ξ_S may be obtained from [9]

$$\xi_S = \sqrt{\frac{\hbar D_s}{2\pi k_B T_{cs}}} = \sqrt{\frac{\xi_{\rm BCS} l}{3.4}}\,. \qquad (1)$$

Using $\xi_{\rm BCS} = 0.18\hbar v_F/k_B T_{cs} = 407$ Å for Nb, we estimate $\xi_S = 115$ Å for the $d_{\rm Gd} = 6$–24 Å series and $\xi_S =$ 130 Å for the $d_{\rm Gd} = 9$–36 Å series. This longer coherence length for the second series makes the Nb layers effectively thinner when considering the overall reduction of T_c due to magnetic pair breaking and may explain the slight discrepancies in T_c. This probably arises from the inevitable slight variation in the deposition conditions from run to run and further illustrates the importance of making wedge films so that samples within a series are internally consistent.

We have attempted to analyze the data in Fig. 4 using the theory of Radović *et al.* [9]. There are three material-dependent parameters in this theory: the coherence length ξ_S, the penetration depth in the magnetic layer ξ_M, and η, which is related to the interfacial scattering. Unlike ξ_S, ξ_M and η cannot be determined separately and must be obtained from a fit. The dashed line in Fig. 4(a) is the best fit we have obtained for the data with $d_{Gd} > 10$ Å (solid squares). Fixing $\xi_S = 145$ Å, the value determined from Eq. (1), we find $\xi_M = 13.5$ Å and $\eta = 0.013$. The qualitative features of the data are reproduced quite well by the model, most notably the maximum in T_c near $d_{Gd} = 20$ Å, which is the signature of the π phase.

There are several discrepancies, however, between the model and the data. At the first minimum in the T_c vs d_{Gd} curve, the model gives a value for T_c that is roughly equal to T_c ($d_{Gd} = \infty$), which we do not observe. This is particularly true for the data in Fig. 4(b), for which a fit as good as that in Fig. 4(a) could not be obtained. In addition, the model does not describe the data well for $d_{Gd} < 10$ Å. This is presumably because these very thin layers are not ferromagnetic, and pair-breaking mechanisms other than those included in the theory become important. A theoretical treatment that includes magnetic fluctuations may be necessary for a full description of these effects. The theory also predicts that the T_c oscillations increase as d_{Nb} decreases, and we do see a somewhat larger effect for $d_{Nb} = 500$ Å than for $d_{Nb} = 600$ Å. At $d_{Nb} = 400$ Å, however, while the initial drop in T_c is larger than in the thicker samples as predicted, the oscillations are much smaller. More generally, the Usadel equations upon which these calculations are based are obtained from the semiclassical theory of superconductivity. For thin layers the approximations inherent in this approach may begin to break down, and a more detailed microscopic model may be needed.

The oscillations in T_c observed in this work are a new feature of superconductor/ferromagnet multilayers. These results provide evidence that a π junction may be possible in a system made from a conventional superconductor. Experiments probing possible spontaneous persistent currents as well as other materials that may show similar effects are under way to explore further the properties of superconductor/ferromagnet structures.

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