Possible Origin for Oscillatory Superconducting Transition Temperature in Superconductor/Ferromagnet Multilayers

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We have studied superconducting and magnetic properties of sputtered Fe/Nb/Fe trilayers. For a fixed Nb thickness and with changing Fe thickness, d_{Fe}, a nonmonotonic behavior of the superconducting transition temperature T_c was observed with a maximum at $d_{\mathrm{Fe}} \approx 10$ Å. The analysis of the magnetization data revealed that for $d_{\mathrm{Fe}} \leq 7$ Å the Fe layer is nonmagnetic. The interpretation of the observed T_c behavior is attributed to the existence of this magnetically "dead" layer and the change of the interaction of the Cooper pairs with this layer at the onset of ferromagnetism for $d_{\mathrm{Fe}} \geq 7$ Å. [S0031-9007(96)01049-6]

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Since the advent of metal superlattice growth capabilities, the possibility to study proximity effects between layers with dissimilar intrinsic properties, such as superconductivity and ferromagnetism, has initiated much research activity [1]. For ferromagnetic (FM) layers sandwiched between superconducting (SC) layers it is expected that the critical temperature for the SC transition T_c decreases monotonically with increasing magnetic layer thickness. Interest in this topic increased considerably after Wong *et al.* [2] showed a nonmonotonic dependence of T_c as a function of the Fe layer thickness in V/Fe superlattices and with fixed V thickness. Shortly afterwards, the possibility for oscillation of T_c as a function of the FM layer thickness in SC/FM multilayers was demonstrated theoretically [3]. It was shown that at specific FM layer thicknesses the Josephson coupling between two SC layers can lead to a junction with an intrinsic phase difference $\Delta\phi = \pi$ which, in turn, exhibits a higher T_c in comparison to the ordinary $\Delta\phi = 0$. Such so-called π junctions have been suggested earlier to arise also in the tunnel barriers containing magnetic impurities [4] and have been proposed recently for weak links of superconductors with d-wave pairing [5]. Although numerous experimental results were discussed in terms of π junctions, any unequivocal observation of π junction coupling has not yet been published.

The evidence for π coupling in SC/FM multilayers was sought experimentally in V/Fe [6], Nb/Gd [7,8], and Nb/Fe [9] systems. In V/Fe [6], contrary to the previous results [2], T_c oscillations as a function of the iron thickness d_{Fe} were not observed. Negative results were also published for the Nb/Fe system [9]. At the same time, for Nb/Gd, a nonmonotonic dependence of T_c on the FM Gd-layer thickness d_{Gd} for fixed d_{Nb} values was reported by Strunk *et al.* [7] and by Jiang *et al.* [8]. For the explanation of the nonmonotonic T_c behavior two different models were proposed. Strunk *et al.* assumed that the obtained T_c behavior could be attributed to the change in the underlying pair-breaking mechanism due to the transition of the Gd layer from a paramagnetic to a FM state with increasing d_{Gd}. In contrast, Jiang *et al.* suggested that the oscillatory T_c behavior provides evidence for the predicted π coupling in SC/FM multilayers.

In order to test the validity of these ideas, we prepared Fe/Nb/Fe-trilayer samples consisting of one single SC layer between two FM layers. Nevertheless, we observed a nonmonotonic T_c dependence on the d_{Fe} at fixed d_{Nb}, which looks very similar to the T_c behavior in Nb/Gd multilayers as reported by Jiang *et al.* [8]. Contrary to their interpretation, we conclude that the nonmonotonic $T_c(d_{\mathrm{Fe}})$ dependence occurs due to the existence of magnetically "dead" Fe layers near the interface and their properties changing drastically upon the onset of FM order.

The samples were prepared by rf sputtering techniques on Al_2O_3 $(11\bar{2}0)$ substrates at 300 K. Pure Ar (99.999%) at pressures of 5×10^{-3} mbar was used as a sputter gas. Very pure Nb (99.99%) and Fe (99.99%) targets were used for deposition. The growth rate was controlled by a quartz crystal monitor, and a rate of 0.1 Å/sec was found to be optimal for the structural quality of the films.

To find the optimal growth conditions for the Fe/Nb/Fe trilayers, systematic resistivity measurements on single Nb films deposited under different conditions were performed. The T_c value and the residual resistivity $\rho(10\ \mathrm{K})$ were observed to be extremely sensitive to the preparation conditions. The highest obtained T_c for a single Nb film with $d_{\mathrm{Nb}} = 400$ Å was 7 K. For this film $\rho(10\ \mathrm{K}) \simeq 13\ \mu\Omega$ cm, decreasing monotonically with increasing d_{Nb}. This probably shows that the conduction electron scattering at grain boundaries is the main scattering process, because usually (see, e.g., [7] and references therein) the mean grain size is roughly proportional to the film thickness. We suppose that this scattering also leads to the so-called lifetime "broadening" of the electronic density of states [10] and to a correspondingly low T_c value (for pure bulk Nb $T_c = 9.2$ K).

In order to study carefully the dependence of the SC parameters on the thickness d_{Fe}, it is essential that the samples are deposited in an identical fashion. Therefore sets of nine different Fe/Nb/Fe trilayer samples with different d_{Fe} at constant d_{Nb} were prepared within one run. Prior to the sample growth, a Nb layer of 30 Å thickness was deposited on the sapphire substrates as a buffer layer. After the deposition process all samples were covered with a protective Nb cap layer of 30 Å thickness.

In Fig. 1 x-ray reflectivity scans measured with Mo $K\alpha_1$ radiation for three trilayers with different d_{Fe} and fixed d_{Nb} are shown. Fits with the Parratt formalism [11] show surface and interface roughnesses of less than 6 Å, indicating the high structural quality of our films. The film thickness obtained from the fit procedure coincides within 10%, with the thickness determined by the quartz crystal monitor during deposition. Using the Parratt fit, we also checked the d_{Nb} values within one set prepared simultaneously and did not find any scatter within the error bar of the fit of about 1%.

Magnetization measurements by a SQUID magnetometer did not indicate qualitative differences in the magnetization curves for samples with a d_{Fe} between 25 and 10 Å at fixed $d_{Nb} = 400$ Å. The hysteresis loops show the typical square shape for ferromagnets and a coercive force $H_c \approx 200$ Oe. The dependence of the saturation magnetization M_s on the reciprocal thickness of the Fe layers is shown in Fig. 2. For the samples with $d_{Fe} \leq 7$ Å there is no contribution to the magnetization from the Fe layers. These results clearly show that a Fe layer of less than 7 Å thickness sandwiched between two Nb layers is nonferromagnetic. The same thickness of a magnetically dead Fe layer was obtained by Mattson *et al.* [12] in their sputtered Fe/Nb superlattices.

The SC transition temperatures T_c were measured resistively in a standard four-terminal configuration and defined at the midpoint of the SC transition. In addition, ac magnetic susceptibility measurements were used to determine T_c for all samples. In this case the temperature corresponding to half the value of the transition signal was defined as T_c. Figure 3 shows the SC transitions observed by electrical resistivity and ac magnetic susceptibility measurements for four samples with different d_{Fe}. These sharp transitions confirm the high quality of our trilayer systems.

The T_c dependence on the Fe thickness obtained for two sets of trilayers with fixed $d_{Nb} = 400$ Å is shown in Fig. 4. A strong initial T_c depression is observed up to $d_{Fe} = 7$ Å. For larger d_{Fe} T_c increases markedly, reaching a maximum at $d_{Fe} \approx 10$ Å and then starts to decrease with a tendency of saturation for $d_{Fe} \geq 20$ Å. We have observed similar nonmonotonic T_c behavior for two sets of samples with $d_{Nb} = 350$ and 450 Å, respectively. It should be emphasized that the maximum of T_c at $d_{Fe} \approx 10$ Å is outside of any possible experimental error bar.

The most important result in our present study is the pronounced maximum of T_c at $d_{Fe} \approx 10$ Å (Fig. 4). As mentioned above, Jiang *et al.* [8] obtained results very similar to ours and interpreted them as the first evidence of π coupling in SC/FM multilayers [3]. Principally, one could assume that the coupling of the main SC Nb layer of our trilayer system with very thin Nb cap and bottom layers might give rise to a π-coupling effect, too. However, we can rule out this explanation for the following reasons: First we note that the difference in

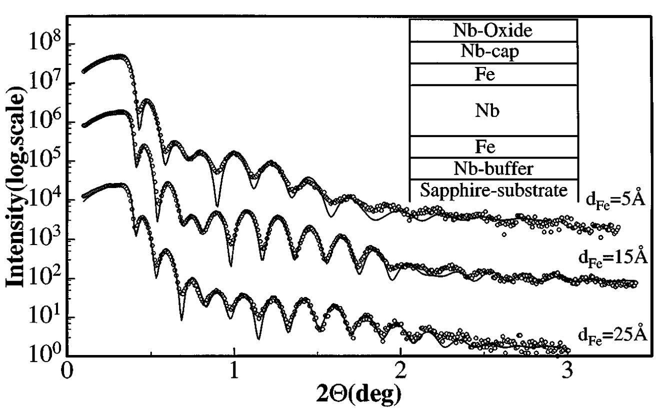

FIG. 1. X-ray reflectivity scans measured with Mo $K\alpha_1$ radiation for trilayers with different d_{Fe} and fixed $d_{Nb} = 100$ Å. The thicknesses of the Nb buffer and cap layer was 30 Å each. The solid line is obtained by model calculations using the Parratt formalism [9]. The multilayer structure is shown in the inset.

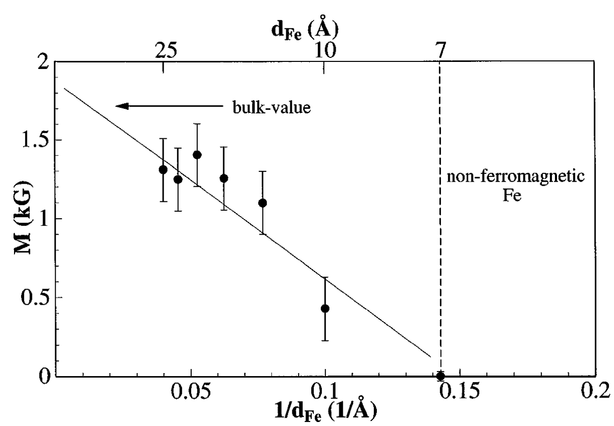

FIG. 2. Saturation magnetization measured by a SQUID magnetometer at 10 K vs $1/d_{Fe}$ for the samples with fixed $d_{Nb} = 400$ Å. The solid line is a linear fit. Note that the sample with $d_{Fe} = 7$ Å was measured with higher precision.

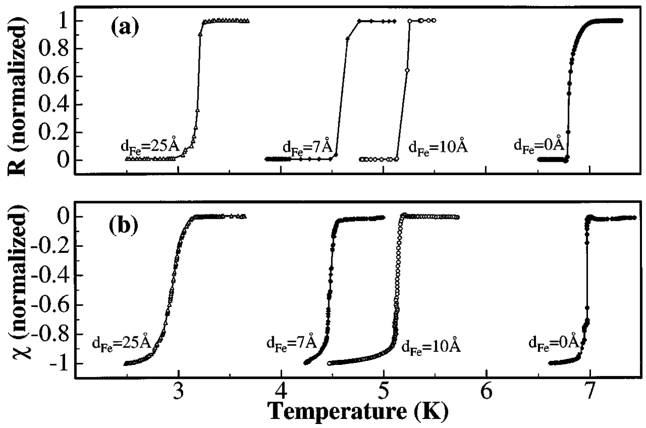

FIG. 3. Superconducting transition curves for samples with different d_{Fe} and fixed $d_{Nb} = 400$ Å measured by electrical resistivity (a) and ac susceptibility (b).

the free energy as well as in T_c between a conventional and π-phase contact of two SC layers SC(1)/FM/SC(2) must vanish as d_1/d_2 in the limit $d_1 \ll d_2$ [here d_1 and d_2 denote the thicknesses of the SC(1) and SC(2)]. For our samples the ratio d_1/d_2 is of the order of 0.1. This makes the π junction effect irrelevant in our case, even if assuming a difference between maximum and minimum in $T_c(d_{Fe})$ caused by π coupling of the order of 1 K for a contact with $d_1 = d_2$. In addition, the amplitude of the order parameter in the top and bottom layers is expected to be strongly reduced by the lifetime broadening effect in thin Nb layers [13].

We believe that the most essential feature of FM/SC multilayers in which a nonmonotonic T_c behavior was observed is the disappearance of ferromagnetism below a critical thickness of the FM layers. We have shown in Fig. 2 that ferromagnetism vanishes at $d_{Fe} \leq 7$ Å in our

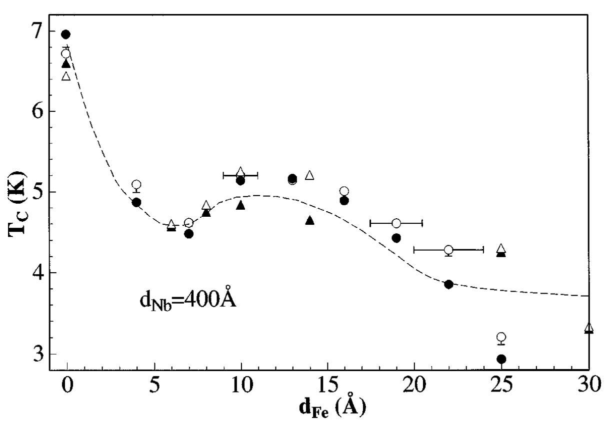

FIG. 4. T_c vs d_{Fe} as determined by ac susceptibility (closed symbols) and resistivity (open symbols) measurements for samples with fixed $d_{Nb} = 400$ Å. The triangles and circles correspond to two different sample sets. The dashed line is a guide for the eye.

Fe/Nb/Fe trilayers, for the Nb/Gd system FM vanishes for $d_{Gd} \leq 12$ Å [7,8]. We suppose that the disappearance of FM order is due to alloying effects at the interface, since the value of the critical thickness is of the same order as the interfacial roughness obtained by the Parratt fit. Principally, the nonferromagnetic layers might be in a paramagnetic or in a nonmagnetic state. In our opinion, in either case it can cause the observed nonmonotonic T_c behavior.

First of all we shall discuss the case when the intermixed layer has localized moments but is in a paramagnetic state. It is obvious that this situation is realized in the Nb/Gd system due to the stability of the $4f$ magnetic moment of the Gd^{3+} ion. In this case we expect a strong initial T_c depression with increasing magnetic layer thickness due to the proximity with the localized moments in the interface area [14] (analogous to the Abrikosov-Gor'kov mechanism of pair-breaking scattering in dilute magnetic alloys [15]). The appearance of FM order within the intermixed region when increasing the magnetic layer thickness will lead to an induced magnetic ordering of the whole intermixed area with a subsequent freezing out of the elastic spin-flip exchange scattering process of the conduction electrons in this region. This gives rise to a sudden increase in T_c; when further increasing the magnetic layer thickness another basic mechanism of T_c depression due to the exchange field at the interface starts to come into play [3].

In our case the intermixed layer is most likely in the nonmagnetic state. We have analyzed the magnetic state of the Fe atoms close to the interface by high resolution magnetization measurements of a single Nb film and of a sample with $d_{Fe} = 7$ Å. In the temperature range from 10 to 100 K and in a magnetic field up to 2500 Oe the magnetic susceptibility values were equal within the experimental error bars for both samples. We estimated that the maximum value of the error is a factor of 2 smaller than the expected magnetic susceptibility of paramagnetic Fe ions incorporated in the interface region. Moreover, in all measurements the scatter of the data points showed that the paramagnetic contribution to the magnetic susceptibility of the Fe/Nb/Fe trilayer is smaller than the magnetic susceptibility of a single Nb film. Therefore we conclude that in our system the interface area for $d_{Fe} \leq 7$ Å is nonmagnetic in accordance with Mössbauer results by Chien *et al.* [16].

The nonmagnetic state of the intermixed layer can easily be understood by the concept of virtual (resonant) d levels [17], formed by Fe ions dissolved in the host Nb metal. Strong mixing of d states with the host band suppresses the local moment of the Fe ions and leads to the appearance of resonant states near the Fermi level. Although these local virtual states are not usual pair breakers, since their contribution to elastic spin scattering is small, they strongly suppress superconductivity by inducing repulsive interactions between the conduction electrons. The origin of this repulsion is the inelastic scattering of electrons on spin fluctuations of Fe-derived resonant levels. The scale for this local paramagnon mediated repulsion can roughly be estimated as $n\lambda^2\tau_{\mathrm{sf}}$, where n is the density of Fe ions in the intermixed region, λ is the coupling constant of the conduction electrons to d-spin density on the resonant level, and τ_{sf} is the characteristic time scale for spin fluctuations on Fe ions.

Let us imagine that the layers with such resonant states form a trilayer system with the SC layer. In this case the Cooper limit for proximity systems works, with T_c given by de Gennes [18], as follows:

$$T_c = 1.14\theta_D \exp\left(-\frac{N_1(\varepsilon_f)d_1 + N_2(\varepsilon_f)d_2}{N_1^2(\varepsilon_f)V_1d_1 + N_2^2(\varepsilon_f)V_2d_2}\right), \quad (1)$$

where the subscripts 1 and 2 refer to the two materials, $N_i(\varepsilon_f)$ is the electronic density of states at the Fermi level, V_i is the electron-electron interaction constant, and d_i is the layer thickness. Since this formula is strictly valid only for $d_i < \xi_i$, in order to sense the characteristic parameters of the interface area we consider the initial T_c depression for a Nb thickness $d_1 = 100$ Å. We took for Nb layer $V_1 = 0.0816$ eV, $N_1 = 3.07$ states/eV, $\theta_D = 325$ K. Assuming $N_2 = N_1$, we estimated $V_2 = 0.046$ eV. Bearing in mind our assumption about the Nb layer thickness, we conclude that the real value of V_2 at the interface of our system is somewhat smaller. Such a weakening of net attraction in the interface region due to electron-paramagnon coupling is not unrealistic.

The above discussion may qualitatively explain the large initial $T_c(d_{\mathrm{Fe}})$ depression in Fig. 4, but the T_c jump at $d_{\mathrm{Fe}} \approx 10$ Å still remains unexplained. We have concluded that above $d_{\mathrm{Fe}} = 7$ Å a FM Fe layer occurs in the middle of the dead Fe layer. This induces a strong internal field and a Zeeman splitting of the resonant d levels in the intermixed region. Concomitantly local spin fluctuations discussed above become strongly suppressed. Then the repulsion between the electrons also decreases, causing an increase of T_c.

In summary, we have studied in detail the magnetic and SC properties of FM/SC/FM triple layer system using Fe/Nb/Fe samples as an example. The first conclusion from our results is that the experimental finding of Jiang *et al.* [8] cannot be taken unambiguously as an evidence for the existence of a π coupling [3]. Second, we deduced that in Fe/Nb/Fe trilayers the nonmonotonic behavior in $T_c(d_{\mathrm{Fe}})$ occurs due to the existence of a magnetically dead Fe-rich layer near the Nb/Fe interface. It is argued that the effective electron-electron attractive interaction in this layer is weakened considerably, giving rise to a strong initial T_c depression up to $d_{\mathrm{Fe}} = 7$ Å. For larger d_{Fe} the appearance of a FM layer within the magnetically dead layer moderates the destructive effect on superconductivity. This is due to the suppression of spin fluctuations mediating the repulsion between electrons by the induced internal field. This leads to an increase of the T_c value. With further increase of d_{Fe} the ordinary T_c depression by the exchange field of the FM layer becomes predominant.

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