Ferromagnetic/superconducting proximity effect in $La_{0.7}Ca_{0.3}MnO_3/YBa_2Cu_3O_{7-\delta}$ superlattices

Z. Sefrioui,[1] D. Arias,[1,*] V. Peña,[1] J. E. Villegas,[2] M. Varela,[1] P. Prieto,[3] C. León,[1] J. L. Martinez,[4] and J. Santamaria[1,†]
[1]*GFMC, Departamento de Fisica Aplicada III, Universidad Complutense de Madrid, 28040 Madrid, Spain*
[2]*Departamento de Fisica de los Materiales, Universidad Complutense de Madrid, 28040 Madrid, Spain*
[3]*Departamento de Física, Universidad del Valle A. A. 25360 Cali, Colombia*
[4]*Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Cantoblanco, Spain*

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We study the interplay between magnetism and superconductivity in high-quality $YBa_2Cu_3O_7$(YBCO)/$La_{0.7}Ca_{0.3}MnO_3$(LCMO) superlattices. We find evidence for the YBCO superconductivity depression in the presence of the LCMO layers. We show that due to its short coherence length, superconductivity survives in the YBCO down to a much smaller thickness in the presence of the magnetic layer than in low T_c superconductors. We also find that for a fixed thickness of the superconducting layer, superconductivity is depressed over a thickness interval of the magnetic layer in the 100 nm range. This is a much longer length scale than that predicted by the theory of ferromagnetic/superconducting proximity effect.

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The ferromagnetic (F)/superconducting (S) proximity effect has been a subject of intense research in recent years due to the rich variety of phenomena resulting from the competition between both long range orderings. In this context F/S superlattices have been extensively used in the past because they offer the possibility of tailoring individual thicknesses or modulation length to match characteristic length scales governing ferromagnetism, superconductivity, or their interaction. Most research in this field has involved single element or alloy-based metallic superlattices.[1–9] The extension of concepts of the F/S proximity effect to the high-T_c superconductors (HTS) or colossal magnetoresistance (CMR) oxides is of primary interest since peculiarities like the short superconducting coherence length and full spin polarization could open the door to interesting new effects. Although there has been a theoretical effort recently to examine the F/S interface in oxides,[10] to the best of our knowledge experimental results on the F/S proximity effect are lacking in the literature. In this paper we examine the interplay between magnetism and superconductivity in $YBa_2Cu_3O_7$(YBCO)/$La_{0.7}Ca_{0.3}MnO_3$(LCMO) superlattices and provide evidence for superconductivity depression due to the presence of magnetic layers. YBCO and LCMO have oxide perovskite structure with very similar in-plane lattice parameters, which allows the growth of superlattices with sharp interfaces, thus strongly reducing extrinsic (structural) effects which otherwise could obscure the F/S interplay.

At the F/S interface, Cooper pairs entering the ferromagnet from the superconductor experience the exchange interaction, which favors one of the spin orientations. This causes the superconducting order parameter to decay in the F layer faster than in a normal metal, within a length scale $\xi_F = \hbar v_F/\Delta E_{ex}$ (where v_F is the Fermi velocity and ΔE_{ex} is the exchange splitting). In single element or alloy ferromagnets, for typical values of $\Delta E_{ex}=1$ eV and v_F of 10^8 cm/s, ξ_F is of the order of 1 nm (Ref. 3), which is shorter than the superconducting coherence length of the low-temperature superconductors (usually larger than 10 nm). Superconductivity is also depressed in the S layer within a characteristic length scale ξ_S, given by $(\hbar D_S/k_B T_c)^{0.5}$,[8] where D_S is the electron diffusion coefficient for the superconductor. ξ_S is of the order of the superconducting coherence length. Thus, the critical temperature of the superlattice can be much smaller than that corresponding to the bulk superconductor. For F/S superlattices, this results in a critical thickness of the superconducting layer d^S_{cr}, below which superconductivity is suppressed. The thickness of the F layers tunes the coupling between the S layers, yielding a critical F layer thickness $d^F_{cr}(\sim 2\xi_F)$, above which the superconducting critical temperature should become independent of the thickness of the magnetic layer (decoupled S layers). Many experimental data on metallic (single element) samples have been analyzed using the theoretical approach by Radovic *et al.*[8] based on Usadel equations[11] and in the de Gennes–Werthammer boundary conditions.[12] Within the framework of this theory, quite exotic phenomena have been predicted and experimentally observed[13–17] for thin magnetic layers, such that the superconducting layers are coupled ($d^F < d^F_{cr} \sim 2\xi_F$). A π phase shift of the order parameter between the superconducting layers yields an oscillating order parameter along the direction normal to the interface, which also gives rise to oscillating dependence on the F layer thickness of T_c, critical currents, and critical fields.

In our system, due to the short YBCO coherence length (0.1–0.3 nm), S layers are expected to sustain superconductivity down to a much thinner thickness than in the case of conventional (low-temperature) superconductors. On the other hand, the F material LCMO shows a large exchange splitting (3 eV) and relatively small bandwidth, giving rise to a fully spin-polarized conduction band,[18] which may suppress superconducting proximity effect into LCMO over very short length scales (small ξ_F). The high-quality LCMO/YBCO superlattices used in this work allow us to investigate both issues.

Samples were grown in a high-pressure (3.4 mbar) pure oxygen sputtering system at high temperatures (900 °C). Individual YBCO films on STO (100) were epitaxial with T_c of 90 K and transition widths smaller than 0.5 K. Growth conditions, optimized for the YBCO, yielded LCMO single films

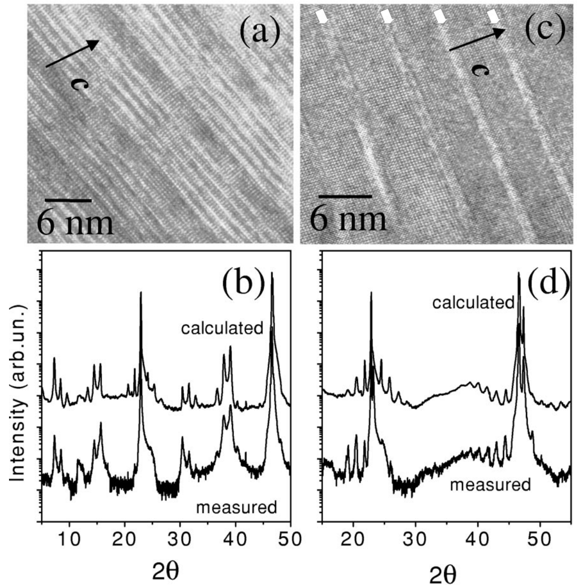

FIG. 1. (a) TEM cross section view of a [LCMO (3 unit cell)/YBCO (5 unit cell)] superlattice. (b) X-ray diffraction pattern and SUPREX calculated spectra of sample [LCMO (3 unit cell)/YBCO (5 unit cell)]. (c) TEM cross section view of a [LCMO (15 unit cell)/YBCO (1 unit cell)] superlattice. (d) X-ray diffraction pattern and SUPREX calculated spectra of sample [LCMO (15 unit cell)/YBCO (1 unit cell)].

with a ferromagnetic transition temperature $T_{CM}=200$ K, and a saturation magnetization $M_S=400$ emu/cm^3, close to the bulk value. Two sets of samples were grown for this study: superlattices with fixed YBCO thickness (5 unit cells per bilayer) and changing LCMO thickness between 1 and 100 unit cells (set A) up to a total thickness of 150 nm; and superlattices with fixed LCMO thickness (15 unit cells) and changing YBCO thickness from 1 to 12 unit cells (set B). Samples were checked for the simultaneous presence of magnetism and superconductivity[19,20] by transport (resistivity) and susceptibility superconducting quantum interference device (SQUID) measurements.

Figure 1 shows x-ray diffraction (XRD) patterns of a sample with very thin YBCO (1 unit cell) and of a sample with very thin manganite (3 unit cells). The corresponding transmission electron microscope (TEM) cross section views of the same superlattices, obtained in a Philips CM200 microscope operated at 200 kV are also shown. Clear superlattice Bragg peaks and satellites can be observed, which together with the flat interfaces of the TEM pictures show a high degree of structural order. XRD patterns were checked for the presence of interface disorder using the SUPREX 9.0 refinement software.[21] The calculated spectra, which are really close to the experimental data, only include step disorder at the interface consisting of 0.5–0.7 manganite unit cells. It is worth remarking that x-ray diffraction and high-resolution electron microscopy probe structure over lateral length scales ranging between tens (XRD) and hundreds of nanometers (TEM). We can therefore not ensure the continuity of the layers for distances comparable to sample dimensions. Refinements were consistent with the absence of interdiffusion. In fact, the incorporation of small amounts ($<10\%$) of La or Ca into Y sites considerably deteriorated the agreement between experimental and calculated spectra. We also found no indications of epitaxial mismatch strain (x-ray refinement did not show changes in the lattice parameters along the c direction) as expected from the small lattice mismatch between YBCO and LCMO.

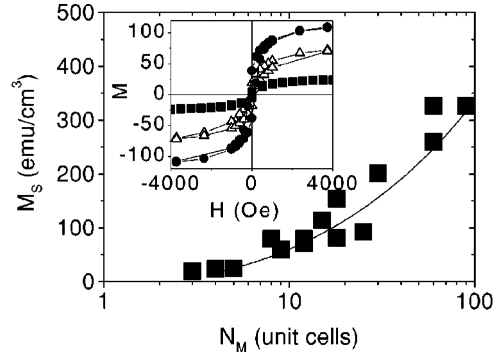

FIG. 2. Saturation magnetization vs LCMO thickness for superlattices [LCMO (N_M unit cell)/YBCO (5 unit cell)]. The line is a guide to the eye. Inset shows hysteresis loops at $T=90$ K for samples with $N_M=5$ (squares), $N_M=12$ (triangles), and $N_M=18$ (circles) unit cells.

The inset of Fig. 2 shows hysteresis loops measured at 90 K (above the superconducting transition) and with magnetic fields parallel to the layers, of samples of set A with 5, 12, and 18 unit-cell-thick LCMO layers. A systematic reduction of the magnetization with LCMO thickness is observed (see main panel of Fig. 2), which has been reported for ultrathin LCMO layers grown on various substrates.[22,23] The inset of Fig. 3 shows resistance curves of representative samples of set A (constant YBCO thickness of 5 unit cells, changing LCMO layer thickness). While the superlattices with thinner LCMO layers show superconducting critical temperatures close to bulk YBCO values, a systematic depression of the critical temperature is observed for samples with LCMO layers thicker than 5 unit cells. The metal insulator transition

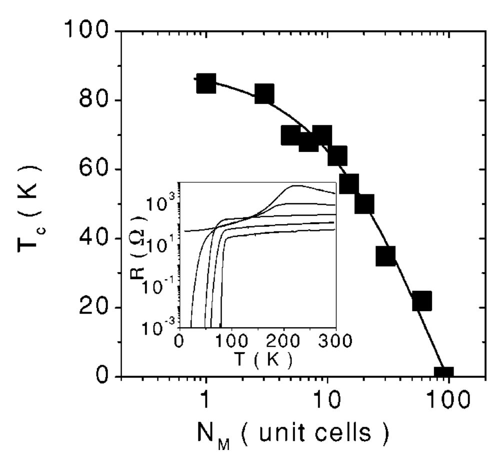

FIG. 3. T_c vs LCMO thickness for [LCMO (N_M unit cell)/YBCO (5 unit cell)] superlattices. Inset: Resistance vs temperature curves for $N_M=3$, 9, 15, 60, 90 unit cells (from bottom to top).

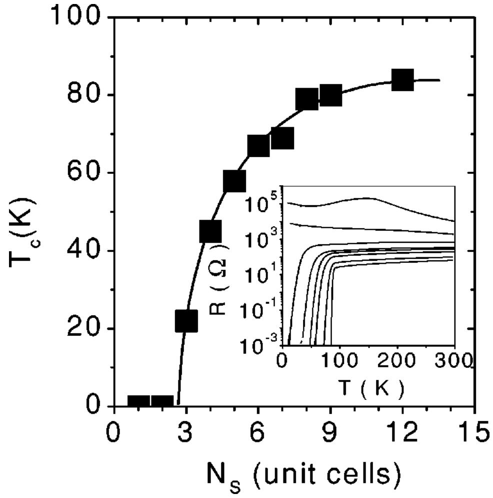

FIG. 4. T_c vs YBCO thickness for [LCMO (5 unit cell)/YBCO (N_S unit cell)] superlattices. Inset: Resistance vs temperature curves for $N_S=1$, 2, 3, 4, 5, 6, 8, 12 (from top to bottom).

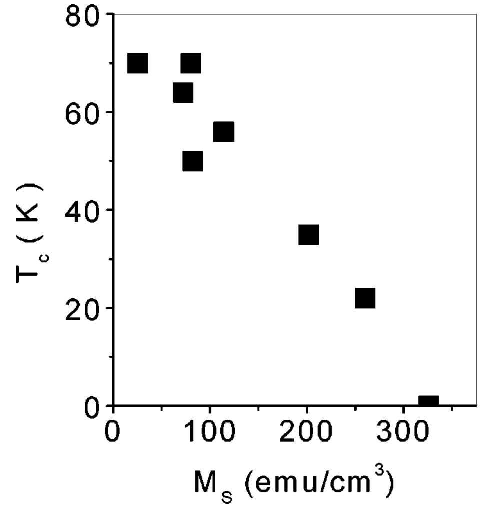

FIG. 5. T_c vs saturation magnetization for [LCMO (N_M unit cell)/YBCO (5 unit cell)] superlattices.

associated to the ferromagnetic transition can be observed in the thicker LCMO layers. Main panel of Fig. 3 shows the evolution of T_c with LCMO layer thickness. T_c is not modified significantly for a LCMO layer thickness up to 3 unit cells. This may be due to suppressed magnetism for the thinnest LCMO layers as reported previously.[22] The question remains how the lateral quality of the interfaces and of the layers may influence magnetic properties of the superlattices. In this respect polarized neutron scattering is a well-suited technique[24,25] to characterize magnetic roughness and its correlation to physical roughness. Future work will be devoted to address this point. However, it is important to notice that T_c keeps on decreasing over a very large LCMO thickness interval. The inset of Fig. 4 shows resistance curves for a series of superlattices with increasing YBCO thickness (set B). It can be observed that the superconductivity is completely suppressed for a YBCO layer thickness of 1 and 2 unit cells. This may result from the discontinuity of the YBCO layers over lateral distances longer than probed by x-ray diffraction and electron microscopy, although it is worth emphasizing that susceptibility measurements also did not show evidence of superconductivity. For larger YBCO layer thickness, however, T_c displays a monotonic increase up to a value of 85 K (close to that of thick single films) for $N=12$. The main panel of Fig. 4 shows the evolution of T_c with YBCO layer thickness.

A depression of the critical temperature of ultrathin YBCO layers (1–5 unit cells) has been also observed in presence of non magnetic spacers of fixed thickness.[26] However we show here that superconductivity is further depressed in presence of the magnetic layers. While 1 unit cell YBCO layer is still superconducting in the presence of 5 unit cells thick $PrBa_2Cu_3O_7$(PBCO) layers in YBCO/PBCO superlattices, with a T_c of 30 K, 1 unit cell of YBCO in the presence of the same thickness (15 unit cells) of LCMO is nonsuperconducting. In addition, 5 unit cells of YBCO in the presence of PBCO have already the bulk T_c, whilst in presence of LCMO a reduced T_c of 50 K is observed. Other extrinsic factors for the depression of T_c such as the deficient oxygenation of the YBCO through the manganite layers can be ruled out since the thickest (above 9 unit cells) YBCO layers almost completely recover the bulk critical temperature (Fig. 4). Moreover, the fact that quite thick LCMO layers are necessary to reduce the T_c of 5 YBCO unit cells supports the idea that the changes of T_c are not due to interdiffusion: if T_c decrease were due to interdiffusion one would expect the greatest effect for the first (few) LCMO unit cells. T_c depression in the presence of the magnetic layers, thus, indicates the interaction between magnetism and superconductivity. In fact, there is an additional result pointing in this direction. We have found a clear correlation between the critical temperature and the magnetic moment of LCMO. Figure 5 shows that the enhanced magnetization of the thicker LCMO layers results in lower T_c values.

We discuss now the possibility of F/S proximity effect in these samples. Due to the F/S proximity effect, the superconducting order parameter within the S layer decays with a characteristic length scale ξ_S, given by $(\hbar D_S/k_B T_c)^{0.5}$.[8] An estimate using the resistivity of the YBCO normal to the CuO planes yields $\xi_S=0.6$ nm, relatively close to the superconducting coherence length, ξ_c (0.1–0.3 nm). In view of Fig. 4, superconductivity is suppressed for a critical thickness $d_{cr}^S\approx 3$ nm (between 2 and 3 unit cells), i.e., $d_{cr}^S/\xi_S \approx 5$ roughly. It is interesting to note that this value of d_{cr}^S is considerably smaller than those found in metallic superlattices with low-T_c superconductors for similar thickness of the magnetic spacer and also for values of the magnetization which are not very different from that of the 15 manganite unit cells. For example, Aarts *et al.*[2] reported $d_{cr}^S=25$ nm for [$V/V_{0.34}Fe_{0.66}$] superlattices and Lazar *et al.*[6] found $d_{cr}^S=70$ nm in Fe/Pb/Fe trilayers, i.e., a much shorter coherence length of YBCO compared to low-T_c superconductors allows superconductivity to exist down to quite small thicknesses in presence of magnetic layers. On the other hand, superconductivity induced within the F layer decays with a length scale $\xi_F=\hbar v_F/\Delta E_{ex}$. Given the large exchange splitting of the LCMO (3 eV) and a Fermi velocity for the majority band of 7.4×10^7 cm/s,[18] the former expression yields very small values for ξ_F of about 0.2 nm. Therefore, the large exchange splitting of the manganite strongly does not support the superconducting proximity effect. In experiments changing the thickness of the magnetic layer (d_F) with fixed thickness of the superconducting layer one expects, according to previous theoretical approaches,[8] that T_c is depressed for magnetic layer thickness smaller than ξ_F, and that T_c saturates at a d_F independent value for a larger thickness of the magnetic layer ($d_F>\xi_F$). Keeping in mind the short values estimated for ξ_F, this is at variance to what is observed in Fig. 3. We have found that T_c is still changing for thicknesses of the magnetic layer which are more than two orders of magnitude larger than the estimated value for ξ_F. In fact more than 50 manganite unit cells (19 nm) are necessary to suppress the superconductivity of 5 YBCO unit cells, suggesting that a much longer length scale than ξ_F is ruling the superconductivity suppression in these oxide systems. The reduced magnetic moment of the thinnest magnetic layers shown in Fig. 5 might be invoked to propose an explanation for the long length scale for superconductivity suppression into the ferromagnet. The exchange splitting ΔE_{ex} is the energy difference between electrons at the Fermi level, with spins parallel or antiparallel to the magnetization. ΔE_{ex} is connected to the magnetic moment μ_F through $\Delta E_{ex}=I_{eff}\mu_F$, where I_{eff} is an effective exchange integral. Thus one expects that ξ_F can be enlarged by the low magnetic moment. In fact $1/\xi_F$ has been shown to increase linearly with magnetic moment of *V*-Fe alloys in *V*/*V*-Fe *F*/*S* multilayers.[2] In our LCMO layers μ_F is reduced by more than 20 times (respect to bulk values) for the thinnest layers and by a factor of 2 for the 50-unit cell-thick LCMO layers. This could explain an apparent enlargement of ξ_F for the thinnest LCMO layers, but still does not explain the decrease of T_c of the 5 unit cells of YBCO of Fig. 3 for the thickest 20–50 LCMO layers.

An additional complication trying to explain Fig. 3 with the *F*/*S* proximity effect is related to interface transparency. From Fig. 3 we find an apparent distance into the ferromagnet (over which T_c is suppressed) which is orders of magnitude longer than the theoretical estimates. Reduced interface transparency due to interface disorder would shorten this distance contrary to what is observed.[27] Moreover, it has been proposed that at the interface with thick half metallic ferromagnets pairs will experience complete reflection due to the energy separation between the bottom of the minority subband and the Fermi level.[2] This is equivalent to a vanishing interface transparency in the formalism of the *F*/*S* proximity effect.[2] It is clear then that the behavior of Fig. 3 cannot be explained by the conventional theory of the *F*/*S* proximity effect. However, we want to remark in this respect that there is no theory for the *F*/*S* proximity effect for fully spin-polarized ferromagnets.

We speculate that the injection of spin-polarized carriers from LCMO into YBCO may add a new source of superconductivity depression: pair breaking by spin-polarized carriers. This mechanism has been theoretically analyzed before[28] and recently observed in manganite/HTS junctions as a depression of the critical current with the injected spin-polarized current.[29,30] The injection of spin-polarized carriers over the superconducting gap depresses the order parameter monotonically with increasing the quasiparticle density. In the simplest picture this depression can be accounted for[31] by

$$\frac{\Delta(n_{qp})}{\Delta(0)}\cong 1-\frac{n_{qp}}{2\Delta(0)N(0)},$$

where $\Delta(n_{qp})$ is the depressed energy gap by the quasiparticle density n_{qp}, $\Delta(0)$ is the zero temperature energy gap, and $N(0)$ is the density of states at the Fermi level. At low temperatures where the thermally induced quasiparticle density is small, recombination of injected spin-polarized carriers requires spin flip scattering what considerably increases their diffusion time. This pair breaking effect extends over the spin diffusion length (l_S) into the superconductor which can be very long; for example, a value of the order of 1 cm has been reported for Al.[32] An estimate of l_S in YBCO can be obtained following Ref. 29, using the relation $l_S=(l_0 v_F \tau_S)^{0.5}$,[30] where τ_S is the spin-polarized quasiparticle diffusion time, v_F is the Fermi velocity, and l_0 is the electron mean free path. Assuming a value of $\tau_S=10^{-13}$ s,[30] $v_F=10^7$ cm/s and that the electron mean free path is limited by YBCO layer thickness $l_0=6$ nm, l_S can be as long as 8 nm. This length scale compares favorably with the thickness of the superconducting layer (6 nm), and suggests that pair breaking by injected spin-polarized carriers could play a role in the superconductivity suppression in our *F*(CMR)/*S*(HTS) superlattices. Further work will be necessary to highlight this point.

In summary, we have provided evidence for superconductivity depression by the presence of the magnetic layer in LCMO/YBCO superlattices. A structural study using x-ray diffraction and electron microscopy has been used to evaluate interface disorder. We have found that YBCO superconductivity is depressed in the presence of manganite layers with a characteristic length scale much longer than that predicted by the existing theories of the *F*/*S* proximity effect. This result should provide an avenue for future theoretical studies of the *F*/*S* proximity effect in presence of spin polarized ferromagnets.

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*On leave from Universidad del Quindio, Armenia, Colombia.
†Corresponding author. Email address: jacsan@fis.ucm.es.

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