Ferromagnetic/superconducting proximity effect in
La$_{0.7}$Ca$_{0.3}$MnO$_3$ / YBa$_2$Cu$_3$O$_{7-\delta}$ superlattices

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Abstract

We study the interplay between magnetism and superconductivity in high quality YBa$_2$Cu$_3$O$_7$(YBCO) / La$_{0.7}$Ca$_{0.3}$MnO$_3$(LCMO) superlattices. We find evidence for the YBCO superconductivity depression in presence of the LCMO layers. We show that due to its short coherence length superconductivity survives in the YBCO down to much smaller thickness in presence of the magnetic layer than in low Tc 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.
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\textsubscript{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 recently a theoretical effort to examine the F/S interface in oxides [10], to the best of our knowledge, experimental results on F/S proximity effect are lacking in the literature. In this paper we examine the interplay between magnetism and superconductivity in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} (YBCO) / La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{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 $\xi_F=hv_F/\Delta E_{ex}$ (where $v_F$ is the Fermi velocity and $\Delta E_{ex}$ the exchange splitting). In single element or alloy ferromagnets, for typical values of $\Delta E_{ex} \approx 1$eV and $v_F$ of $10^8$ cm/s, $\xi_F$ is of the order of 1 nm [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, $\xi_S$, given by \( (hD_S/ k_B T_c)^{0.5} \) [8], where $D_S$ is the electron diffusion coefficient for the superconductor. $\xi_S$ 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
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 frame 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 \((d^F < d_{cr}^F \sim 2\xi_F)\). A \(\pi\) 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 F layer thickness of \(T_c\), critical currents and 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 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 \(\xi_F\)). 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 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 (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 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. 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.

Samples were magnetic down to the smallest LCMO layer thickness. The inset of Figure 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 cells thick LCMO layers. A systematic reduction of the magnetization with LCMO thickness is observed (see main panel of figure 2), which has been reported for ultrathin LCMO layers grown on various substrates [22, 23]. The inset of figure 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 associated to the ferromagnetic transition can be observed in the thicker LCMO layers. Main panel of figure 3 shows the evolution of $T_c$ with LCMO layer thickness. It is important to notice that $T_c$ keeps on decreasing over a very large LCMO thickness interval. The inset of figure 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 YBCO layer thickness of 1 and 2 unit cells. 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. Main panel of figure 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 [24]. 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 presence of 5 unit cells thick PrBa$_2$Cu$_3$O$_7$(PBCO) layers in YBCO / PBCO superlattices, with a $T_c$ of 30 K, 1 unit cell
of YBCO in presence of the same thickness (15 unit cells) of LCMO is non superconducting. In addition, 5 unit cells of YBCO in 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 $T_c$ like 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 (figure 4). Moreover, the fact that quite thick LCMO layers are necessary to reduce the $T_c$ of 5 YBCO unit cells supports 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 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 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 $\xi_S$, 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, $\xi_c$, (0.1-0.3 nm). In view of figure 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., 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 $7.4 \times 10^7$ cm/s [18], the former expression yields very small values for $\xi_F$ of about 0.2 nm. Therefore, the large exchange splitting of the manganite strongly unfavors 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 Tc is depressed for magnetic layer thickness smaller than ξ_F, and that Tc saturates at a d_F independent value for larger thickness of the magnetic layer (d_F > ξ_F). Keeping in mind the short values estimated for ξ_F, this is at variance to what is observed in figure 3. We have found that Tc 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 figure 5 might be invoked to propose an explanation for the long length scale for superconductivity suppression into the ferromagnet. The exchange splitting ∆E_{ex} is the energy difference between electrons at the Fermi level, with spins parallel or antiparallel to the magnetization. ∆E_{ex} is connected to the magnetic moment µ_F through ∆E_{ex}=I_{eff} µ_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/ξ_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 thick 50 unit cells LCMO layers. This could explain an apparent enlargement of ξ_F for the thinnest LCMO layers, but still does not explain the decrease of Tc of the 5 unit cells of YBCO of figure 3 for the thickest 20-50 LCMO layers.

An additional complication trying to explain the figure 3 with the F/S proximity effect is related to interface transparency. From figure 3 we find an apparent distance into the ferromagnet (over which Tc 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 [25]. 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 figure 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 not a theory for the F/S proximity effect for fully spin polarized ferromagnets.

We speculate that the injection of spin polarized carriers from the LCMO into the YBCO
may add a new source of superconductivity depression: pair breaking by spin polarized carriers. This mechanism has been theoretically analyzed before [26] and recently observed in manganite/HTS junctions as a depression of the critical current with the injected spin polarized current [27, 28]. 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 [29] by \( \Delta(n_{qp}) \approx 1 - \frac{n_{qp}}{2\Delta(0)N(0)} \) where \( \Delta(n_{qp}) \) is the depressed energy gap by the quasiparticle density \( n_{qp} \), \( \Delta(0) \) is the zero temperature energy gap and \( N(0) \) 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 [30]. An estimate of \( l_S \) in YBCO can be obtained following ref. 27, using the relation \( l_S = (l_0 v_F \tau_S)^{0.5} \) [28], where \( \tau_S \) is the spin polarized quasiparticle diffusion time, \( v_F \) is the Fermi velocity and \( l_0 \) the electron mean free path. Assuming a value of \( \tau_S = 10^{-13} \) s [28], \( v_F = 10^7 \) 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 TEM and x ray refinement has been used to discard extrinsic effects like interface disorder or interdiffusion. We have found that YBCO superconductivity is depressed in 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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FIGURE CAPTIONS

**Figure 1:** (a) TEM cross section view of a [LCMO (3 u.c.)/YBCO (5 u.c.)] superlattice. (b) X-Ray diffraction pattern and SUPREX calculated spectra of sample [LCMO (3 u.c.)/YBCO (5 u.c.)] (c) TEM cross section view of a [LCMO (15 u.c.)/YBCO (1 u.c.)] superlattice. (d) X-Ray diffraction pattern and SUPREX calculated spectra of sample [LCMO (15 u.c.)/YBCO (1 u.c.)]

**Figure 2:** Saturation magnetization vs. LCMO thickness for superlattices [LCMO (N<sub>M</sub> u.c.)/YBCO (5 u.c.)]. Line is a guide to the eye. Inset shows hysteresis loops at T=90 K for samples with N<sub>M</sub>=5 (squares), N<sub>M</sub>=12 (triangles) and N<sub>M</sub>=18 (circles) unit cells.

**Figure 3:** T<sub>c</sub> vs. LCMO thickness for [LCMO (N<sub>M</sub> u.c.)/YBCO (5 u.c.)] superlattices. Inset: Resistance vs. temperature curves for N<sub>M</sub>=3, 9,15,60,90 unit cells (from bottom to top).

**Figure 4:** T<sub>c</sub> vs. YBCO thickness for [LCMO (5 u.c.)/YBCO (N<sub>S</sub> u.c.)] superlattices. Inset: Resistance vs. temperature curves for N<sub>S</sub>=1,2,3,4,5,6,8,12 (from top to bottom).

**Figure 5:** T<sub>c</sub> vs. saturation magnetization for [LCMO (N<sub>M</sub> u.c.)/YBCO (5 u.c.)] superlattices.
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Figure 3. Variation of $T_c$ (K) with $N_M$ (unit cells). The inset shows the resistance $R$ ($\Omega$) as a function of $T$ (K).
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Figure 5
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