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## CHARGE TRANSFER PHENOMENA IN $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}/\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ INTERFACES

**M. Varela<sup>1</sup>, V. Peña<sup>2</sup>, Z. Sefrioui<sup>2</sup>, A. R. Lupini<sup>1</sup>, J. Santamaria<sup>2</sup>, S.J. Pennycook<sup>1</sup>**

<sup>1</sup> Oak Ridge National Laboratory, Oak Ridge, TN 37831-6031

<sup>2</sup> GFMC. Dpto. Fisica Aplicada III, Universidad Complutense de Madrid, 28040 Madrid, Spain,

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<sup>1</sup> Oak Ridge National Laboratory, Oak Ridge, TN 37831-6031

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In the last years much attention has been paid to oxide ferromagnetic /superconducting (F/S) heterostructures where a high critical temperature superconductor (HTCS) is combined with a colossal magnetoresistant (CMR) manganite oxide. The full spin polarization in the manganite together with the short coherence length and d-wave superconductivity in HTCS materials are new ingredients (as opposed to conventional F/S systems where a metal is combined with a low  $T_c$  superconductor) which, can have important implications both for basic and applied research. In such oxide heterostructures the interfaces are specially complex, and structural disorder (steps, interdiffusion, alloying, etc) may obscure interaction phenomena between superconductivity and ferromagnetism. Moreover, since CMR and HTCS oxides are extremely sensitive to doping, charge transfer processes at the interfaces could give rise to accumulation or carrier depleted interface layers directly affecting the superconducting and/or magnetic properties of the individual layers.

In this work we study the relation between interface structure and electronic properties at the atomic scale in HTCS/CMR interfaces in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}/\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (YBCO/LCMO) superlattices, by means of high spatial resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). Samples with variable YBCO thickness ( $1 < n < 15$  unit cells) and a constant LCMO thickness of 15 unit cells (5.8

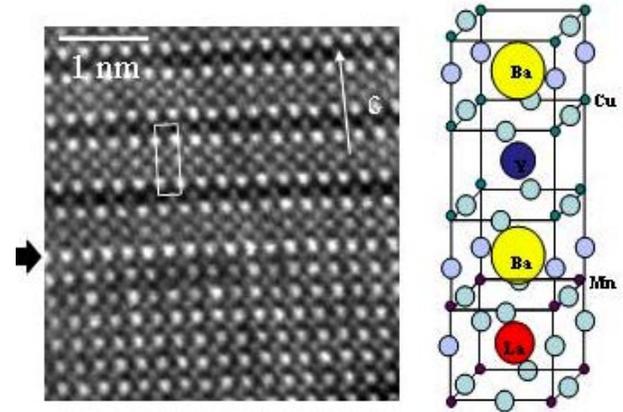


Fig. 1: (Left) High resolution STEM image of a YBCO(top)/LCMO(bottom) interface. The interface has been marked with a black arrow. A rectangle highlights one YBCO unit cell. (Right) (100 nm approx.) were grown by high oxygen pressure sputtering<sup>1</sup>. The excellent lattice match among both materials ( $< 0.5\%$ ) allows excellent quality epitaxial growth. Structure and electronic properties were analyzed in an aberration corrected VG Microscopes HB501UX operated at 100 kV and equipped with a parallel EEL spectrometer.

Low magnification STEM images show that layers are flat and continuous over large lateral distances. Figure 1 shows a high magnification image of an YBCO/LCMO interface from a  $[\text{YBCO}_{10 \text{ u.c.}}/\text{LCMO}_{15 \text{ u.c.}}]_{100 \text{ nm}}$  superlattice. The YBCO/LCMO interface is coherent and free of defects. Occasionally, some steps one unit cell high are observed. The adjacent model in figure 1 shows the

interface structure found. As the LCMO growth ends in a  $\text{MnO}_2$  plane, the YBCO stacking lacks the CuO chains at the interface. The CuO chains are the charge reservoirs in YBCO, and therefore their absence explains the lack of superconductivity in ultrathin YBCO layers (1 or 2 unit cells thick) in YBCO/LCMO superlattices<sup>1</sup>.

Interestingly, spectroscopic measurements with atomic resolution provide evidence for charge transfer effects at the LCMO/YBCO interface through the  $\text{MnO}_2$  interface plane. In YBCO the study of the oxygen K edge (at 530 eV), which results from exciting transitions from the oxygen 1s core level to the oxygen 2p bands, can be used to probe the occupancy of the oxygen 2p bands, i.e. the hole doping. In particular, the intensity of the pre-peak at 528.5 eV (marked with a dotted line in figure 2(a)) correlates with the hole density<sup>2,3</sup>. By placing the electron beam on the interface, and acquiring EEL spectra while moving into the YBCO the carrier density in the YBCO can be mapped with atomic resolution. Figure 2(a) shows the evolution of the oxygen K edge as a function of the distance to the interface, while figure 2(b) shows the pre-peak intensity, i.e. the hole density, again as a function to the distance to the interface. While on the interface YBCO unit cell the density of holes is comparable to the one found in deoxygenated YBCO with 6.4 oxygen ions per unit cell<sup>2,3</sup>, at approximately 3 nm within the YBCO layer the optimal hole doping of bulk YBCO is measured. In between, a smoothly increasing density of holes is found.

This interface hole filling is most likely a result of the transfer of charge from the LCMO layers into the YBCO. Actually, the average Mn formal oxidation state in the LCMO layers, measured also by EELS, is around  $+3.45 \pm 0.10$ . If we have in mind that the nominal chemical doping yields an

average Mn valence of +3.3, around 0.15 electrons per LCMO unit cell may be transferred into the YBCO, giving rise to the observed hole depleted interface layer. This layer could explain the low  $T_c$  values found in YBCO/LCMO superlattices, especially when the YBCO thickness is below 6 unit cells, and should be taken into account when trying to understand the interaction of superconductivity and ferromagnetism in oxide F/S superlattices.

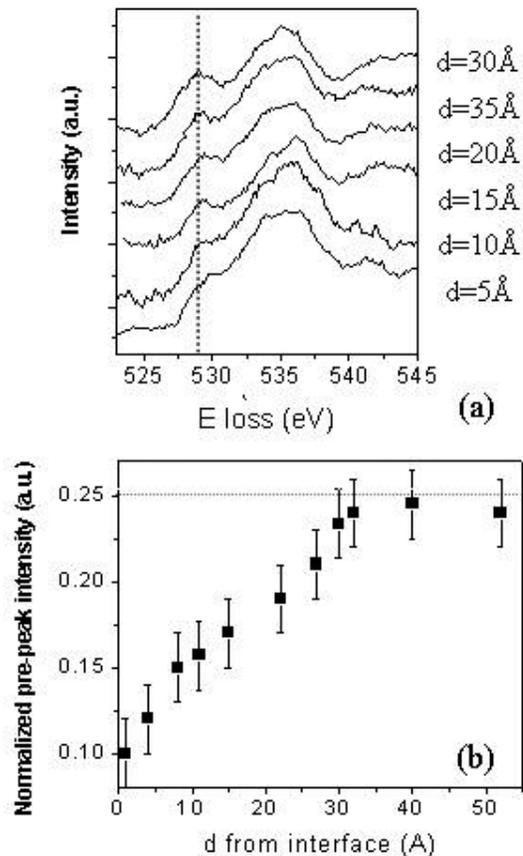


Fig. 2: (a) O K edge variation within the YBCO layer as a function of the distance to the YBCO/LCMO interface. The position of the pre-peak has been marked with a vertical dotted line. (b) Normalized pre-peak intensity within the YBCO, which correlates with the hole density, vs. the distance to the interface. The horizontal dotted line represents the optimal doping value in bulk YBCO.

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