Indirect Electric Field Doping of the CuO$_2$ Planes of the Cuprate NdBa$_2$Cu$_3$O$_7$ Superconductor

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The mechanism of field-effect doping in the 123 high critical temperature superconductors (HTS) has been investigated by x-ray absorption spectroscopy in the presence of an electric field. We demonstrate that holes are created at the CuO chains of the charge reservoir and that field-effect doping of the CuO$_2$ planes occurs by charge transfer, from the chains to the planes, of a fraction of the overall induced holes. The electronic properties of the charge reservoir and of the dielectric-HTS interface determine the electric field doping of the CuO$_2$ planes.

The physical phenomena occurring at the interface between materials having different bulk electronic properties are extremely important in modern electronics [1]. The great success of the metal-oxide semiconductor field-effect transistors is due to the high technological control of the Si/SiO$_2$ interface and to the very good understanding of the electric field-effect mechanisms at the interface between a band insulator and a band semiconductor. Such detailed insight is missing for the interfaces of materials with strong electron correlation, such as the high critical temperature superconductors (HTS).

The application of an electric field at the interface between an insulator and a metal or semiconductor is considered a general method to change reversibly the electronic properties of thin film without introducing chemical and structural disorder. In particular, the electric field effect has been used to shift the critical temperature and even to induce phase transitions in conventional and high critical temperature T_c superconductors [2–7]. Experiments conducted on HTS from the early 1990s to now have been usually interpreted by supposing that the induced charges become carriers in the CuO$_2$ conducting planes, thus changing the filling of the Zhang-Rice (ZR) band [8]. The universal relationship between T_c and the carrier density in the CuO$_2$ planes of the HTS (the so-called HTS dome) [9], suggested that an external electric field could easily lead to controllable changes of their electronic properties. Although modulations of T_c [5,10,11] and of the critical current density [6] were observed in the "123" YBa$_2$Cu$_3$O$_7$ and NdBa$_2$Cu$_3$O$_7$ (NdBCO) thin films, the extent of the electric field effect was found to be below expectations. Superconducting-to-insulating transitions were observed only in samples with a doping exactly at the separation of the two electronic phases [4,7], while small changes on the sample conductivity were observed in Bi$_2$Sr$_{1.5}$La$_{0.5}$CaCu$_2$O$_{8+\delta}$ films having a single insulating CuO$_2$ plane doped in a range nominally spanning the whole HTS dome [12]. As a matter of fact, a direct doping of the superconducting CuO$_2$ planes by the polarization charges created by the electric field has not been clearly demonstrated yet.

Here we present an x-ray absorption spectroscopy (XAS) study of the electric field doping of the well studied SrTiO$_3$/NdBCO interface. The Cu L_3 edge ($2p_{3/2} \rightarrow 3d$ transition) XAS experiment was performed at the ID08 beam line of the European Synchrotron Radiation Facility. It was designed in order to allow simultaneous spectroscopic and transport characterization of the samples under the application of an electric field. Within the wide family of the HTS, NdBCO belongs to the 123 group, where, besides superconducting CuO$_2$ planes, an important role is played by the CuO chains within the "charge reservoir" (CR). Transmission electron microscopy [13] has demonstrated that the first layer at the SrTiO$_3$/NdBCO interface belongs to the CR, as sketched in Fig. 1(a). This is particularly relevant since the effective electric field penetration calculated by a Thomas Fermi model or by any simple electrostatic estimates is of the order of 1 nm or less, i.e., less than one unit cell (u.c.). In previous studies the role of the atomic layers directly facing the interface was largely neglected. In this Letter we will show, on the contrary, that they play a decisive role in the microscopic mechanism of the field-effect doping of cuprates.

NdBCO (001) ultrathin films have been epitaxially grown, by high oxygen pressure diode sputtering, on TiO$_2$ terminated $10 \times 10 \times 0.5$ mm^3 SrTiO$_3$ (100) (STO) surface. The samples are pseudomorphic to the STO single crystals and have high structural perfection, and very smooth surfaces. The field-effect structures have been completed by deposition on the thin film of the gold pads for transport measurements, and of the gate electrode (4×2 mm^2 area) on the back of the substrate, in a geometry suitable for the XAS experiment. The field has been applied through the SrTiO$_3$ single crystal under ultra-high-vacuum conditions. The devices have been characterized *in situ* during the XAS experiment. A negative V_{gate} creates
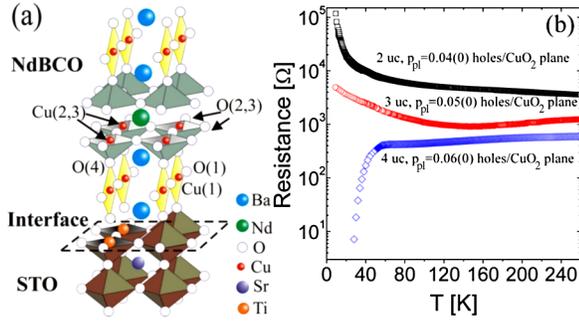
FIG. 1 (color online).   (a) Sketch of the NdBCO/STO interface with the labeling of the inequivalent copper and oxygen sites used throughout the text. The interface plane is shown as a dashed line separating the TiO_2 plane of the STO (100) single crystal from the BaO plane of the NdBCO film. (b) *In situ* measured four point probe channel resistance of the three NdBCO devices: 4 u.c. (blue or dark gray diamonds) superconducting with critical temperature $T_c = 20$ K and carrier density $p_{pl} = 0.06(0)$ holes/CuO_2 plane; 3 u.c. (red or gray circles) and 2 u.c. (black circles) insulating with $p_{pl} = 0.05(0)$ and $0.04(0)$ holes/CuO_2 plane, respectively.

holes at the interface (accumulation mode) and a positive V_{gate} reduces the density of holes in the sample (depletion mode). The capacitance of this device is a function of the gate voltage, a well-known result for nonlinear dielectrics materials like STO. At low gate voltage it is about 2.5 nF and it decreases to 0.4 nF at high voltages. The charge accumulated at the interface is consequently measured by an electrometer and is related to the capacitance and to the areal carrier density Δn_s through the relation $Q = -e \cdot \Delta n_s = \int_0^{V_{gate}} CdV$. With $V_{gate} = \pm900$ V, about $\pm6.0 \times 10^{13}$ holes/cm^2 can be subtracted/added at the STO/NdBCO interface (see also Ref. [14]).

We have studied NdBCO samples with a doping above and below the critical value separating the superconducting and insulating phases [Fig. 1(b)] [15]. An example of the effect of the electric field is shown in Fig. 2. The resistivity of the 3 u.c. NdBCO sample at 10 K nonlinearly decreases as function of Δn_s, in agreement with the induction of carriers in the CuO_2 planes. It is worth nothing that the field-effect doping is insufficient to induce superconductivity. Similarly, we could not revert the 4 u.c. sample from superconducting to insulating by applying a positive gate voltage. These results are in contradiction with simple model expectations: assuming that only one unit cell is doped and that all the carriers are transferred to the CuO_2 planes, about $p_{pl} = 0.05$ holes/CuO_2 plane would be added or subtracted. In the 3 u.c. NdBCO the average hole population per CuO_2 plane is $0.05(0)$, consequently the electric field should bring to zero the conduction carriers for $V_{gate} = +900$ V and double them for $V_{gate} = -900$ V. In such a scenario, an insulating to superconducting transition is expected, as shown in the inset of Fig. 2. Even assuming that all the unit cells are doped, a phase
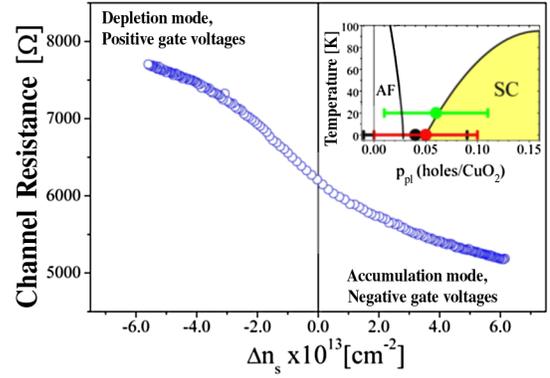
FIG. 2 (color online).   The channel resistance of the 3 u.c. device, measured as a function of the number of holes per unit area induced by the electric field. In the inset T_c vs doping (ppl) characteristics of the 4 u.c. (green or light gray circle), 3 u.c. (red or gray circle) and 2 u.c. (black circle) overlapped to the HTS dome (SC stands for superconducting and AF for antiferromagnetic phases). The horizontal bars around each experimental point are the estimated field effect, in the assumption that all the induced charge become carriers in the CuO_2 planes of the first unit cell at the interface.

transition should occur anyhow in the samples studied, because the carrier density would change by $\Delta p_{pl} = \pm0.015$ holes/CuO_2, i.e., enough to induce a transition.

To unravel the underlying microscopic mechanism of the electric field effect, we have used the XAS technique that is sensitive to the orbital occupation and symmetry at the different copper sites of our samples. We collected the total electron yield signal that probes a depth of few nanometers, slightly larger than the NdBCO film thickness. By using the linear polarization of the x rays, spectra corresponding to final states lying parallel or perpendicular to the CuO_2 planes have been measured (I_{ab} and I_c spectra in Fig. 3; see Ref. [14]).
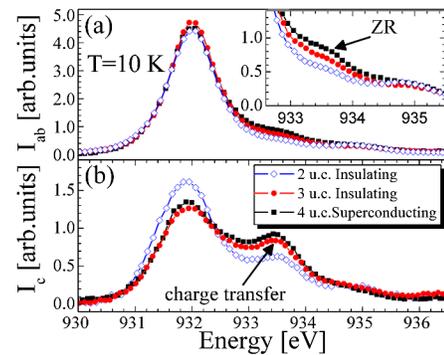
FIG. 3 (color online).   Cu L_3 XAS spectra, with **E**$\|ab$ (I_{ab}) and (b) **E**$\|c$ (I_c), measured at low temperature (10 K). The ZR satellite peak intensity is related to the number of holes per CuO_2 plane (see text). This feature decreases continuously when going from 4 u.c. (black squares) to 2 u.c. (blue or dark gray diamonds), in agreement with transport data.

The Cu L_3 spectra, measured on the NdBCO films at 10 K, present the typical features of all cuprates, i.e., a main peak at 932.0 eV and a shoulder at 933.5 eV (Fig. 3) [16]. 123 cuprates contain two inequivalent copper sites, i.e., Cu(1) in the chains and Cu(2,3) in the CuO$_2$ planes [see Fig. 1(a)]. As shown in [17,18], the main peak has a contribution from the doped Cu(1)$^{3+}$ in the chains that form a ligand state ($3d^9\underline{L}$) with the neighboring oxygen ions, which increases if holes are injected in the chains along the a-b axes. Another contribution comes from the undoped Cu(2, 3)$^{2+}$ in the CuO$_2$ planes ($3d^9$ state). The remaining doped Cu(2,3) sites, occupied by formally trivalent Cu(2, 3)$^{3+}$ ions, give rise to the satellite peak at 933.5 eV. In the I_{ab} spectra, this feature is due to the Zhang-Rice (ZR) singlet [8], i.e., to the mobile carriers in the CuO$_2$ planes. In the I_c spectra the satellite is due to Cu(2, 3)$^{3+}$ sites hybridized with the apical O(4) oxygen, a signature of the charge transfer from the chains to the planes. As shown in Fig. 3 and in [19], the satellite peaks decrease with the thickness of the NdBCO films, in agreement with the transport properties, with the reduction of the carrier density and of the charge transfer from the chains to the CuO$_2$ plane.

The effects of the electric field on the I_{ab} spectra at 10 K are shown in Fig. 4 for the 3 u.c. sample, and similar result were found for the 2 and 4 u.c. films. Under negative (positive) gate voltages, the satellite at 933.5 eV, acquires (looses) spectral weight because the injected charges fill up (empty) the ZR band; i.e., additional carriers appear at the CuO$_2$ planes. However, the largest effects are observed on the main peak, which shows a strong increase (decrease) in intensity and a gradual broadening (narrowing) on the high-energy side. As shown in Fig. 4(b), where the spectrum at zero field is subtracted from the data, a peak at about 932.2 eV continuously grows with negative gate voltages. These results are explained by an enhancement of hole density along the chains by negative fields. The ratio of the holes induced in the chains [at the Cu(1) sites] and in the CuO$_2$ planes [at the Cu(2,3) sites] as estimated from the integrated intensities around 932.2 and 933.5 eV in Fig. 4(b), is 3.5 ± 0.5. It does not depend on the gate voltage within the experimental error.

The electric field effect is similar in the ab plane and along the c axis. However, interesting differences can be noted. In Fig. 4(c) we show the XAS ($I_{ab} - I_c$) spectra as a function of the field: for negative (positive) gate voltages, the main peak at 932 eV acquires (loses) relative in-plane intensity, whereas the satellite anisotropy remains almost unaffected. This confirms that negative voltages lead to a strong enhancement of the hole population along the chains (parallel to the ab plane). On the contrary the filling of the ZR band is accompanied by an equal change of Cu(2,3)-O(4) ligand states. This is a further confirmation that the doping of the CuO$_2$ planes is rather indirect; i.e., it occurs by a partial charge transfer from the heavily doped chains via the Cu(2,3)-O(4) bonding.
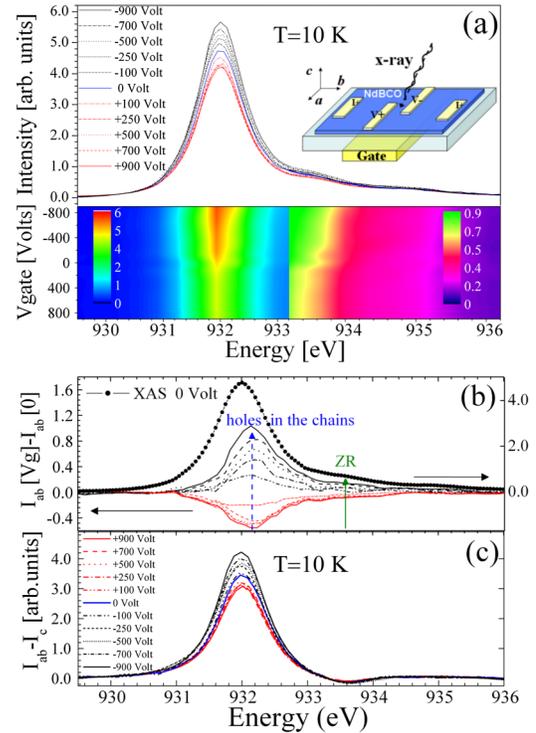
FIG. 4 (color online).   (a) Gate voltage dependence of the I_{ab} XAS spectra in the 3 u.c. NdBCO device (the experimental configuration is shown in the inset): in the upper panel the I_{ab} spectra are shown for negative (black lines) and positive (red or gray lines) gate voltages. The blue or dark gray line is acquired at zero field. In the lower panels the data are shown as color map pictures with different linear color scales around the main peak at 932 eV (left panel) and around the $\underline{c}3d^{10}\underline{L}$ satellite (right panel). (b) Effect of the field shown by subtracting to each I_{ab} XAS spectra the reference scan acquired without the field (black closed and line joined circles). (c) Difference between I_{ab} and I_c XAS spectra at different gate voltages.

The XAS results are consistent with the transport data measured *in situ* and shown in Fig. 2. In particular we find a nonlinear relationship between the change in the resistance and the weight of ZR states (proportional to the integrated intensity of the satellite peak) from $V_{gate} = +1000$ V to -500 V and a saturation (lower slope) at higher negative voltages. This resembles the nonlinear relationship between the resistivity and induced carrier density shown in Fig. 2 and can be explained by taking into account the activated temperature dependence, with a slope depending on the carrier density, of the resistance in insulating cuprates.

The data are also consistent with previously published results. In 123 compounds shifts of T_c up to 10 K where observed in samples not fully superconducting at 4.2 K [10,11]. There the carrier doping at zero field was similar to ours (about 0.05 holes/CuO$_2$ plane) and an increase of about 0.06 holes/CuO$_2$ plane should have been expected at maximum field, corresponding to shift of T_c greater than 30 K, instead of the 10 K observed. In Ref. [4] similar

differences between the measured shift in T_c and the values expected from the injected carrier density are also reported [20].

In conclusion, our experimental results give the evidence that an external electric field injects holes mainly in the chains belonging to the charge reservoir, whereas only a fraction of them are transferred to the CuO_2 planes by charge transfer from the charge reservoir to the CuO_2 planes, which is the same mechanism governing the doping of the CuO_2 planes by chemical substitution in the whole HTS family. This process is specific to the family of 123 compounds, where the CR is composed by CuO chains. However, it is likely that a similar scheme could operate in the case of other HTS; i.e., the electric field could modify the valence of the cations in the CR and in this way could transfer holes to the CuO_2 planes.

The similarity between electric field and chemical doping opens new perspectives for the investigation of the microscopic phase separation phenomena, proposed to be a key ingredient in the description of superconducting to insulator transitions of underdoped HTS [21]. Indeed while the charge induced by field effect is homogeneously distributed within the gate area at the interface with the thin HTS film, the holes created by chemical doping are not, especially in the case of insulating or barely superconducting samples. The apparent similarities between field-effect doping and chemical doping may thus suggest that collective electronic phase separation is necessary to accommodate doped holes in the parent undoped compounds. Further studies in this direction are required to confirm this hypothesis. Finally, our experiment clarifies that, to obtain a shift of T_c of several degrees or a phase transition, a doping level substantially higher than usually achieved is necessary. On the other hand, by having identified the physical mechanisms leading to electric field doping of the CuO_2 planes in the HTS, we have shown that an advanced interface engineering, i.e., the right choice of the atomic layers at the interface and their chemical and structural control, can eventually open the way to a more effective field-effect doping of high critical temperature superconductors.

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