ESRF	**Experiment title:** *Electric field induced effects on the local electronic structure of ultrathin $Nd_{1.2}Ba_{1.8}Cu_3O_y$ films*	**Experiment number**: HE2097
Beamline: ID08	**Date of experiment**: from: 29/11/2006 to: 05/12/2006	**Date of report**: 02/10/2007
Shifts: 18	**Local contact(s)**: N.B. Brookes	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

* Marco SALLUZZO
* Julio Criginski CEZAR
* Gabriella Maria DE LUCA
* Giacomo GHIRINGHELLI
* Francesca FRACASSI

Report:

The high temperature superconductors (HTS) are characterized by a general temperature *vs* number of holes per CuO_2 planes (p_{pl}) phase diagram. The relevance of this experimental finding is a much debated issue but what is very interesting is that according to this feature phase transitions from an antiferromagnetic insulator to a superconductor can be realized by changing the number of carriers. Unfortunately this task is easily accomplished only by change of chemical compositions that introduces a nm scale disorder, like in $La_{1-x}Sr_xCuO_4$. Alternatively the number of holes can be modified using the electric field effect that is very attractive because it is controllable by an accessible external parameter, i.e. a gate voltage of a field effect transistor (FET). The physics of the electric field effect in the strongly electron correlated materials is very poorly understood, that is at odd with the very well studied band insulator/band semiconductor interfaces.

In this experiment we used high resolution, polarization dependent, X-ray Absorption Spectroscopy (XAS) around Cu.L3, O-K and Ba M edges to map the effect of the electric field on the unoccupied density of states of the $SrTiO_3$/ $Nd_{1.2}Ba_{1.8}Cu_3O_7$ (NBCO) interface. To this purpose the sample holder of the ID08 XAS station has been modified in order to allow in situ transport measurements under the application of gate voltages up to 1000 Volts. The devices investigated are composed of thin NdBCO epitaxial film deposited on $SrTiO_3$ single crystal, used as dielectric insulator of the field effect device, of a gate electrode deposited on the back side of the STO, and of four gold contacts with a suitable geometry on the top of the NdBCO film. The electric field is applied through the 0.5 mm STO single crystal on a region of the sample of 4x2 mm^2 area assuring uniform changes of the electronic properties of the film in the region illuminated by the beam. Transport measurements were performed by feeding a constant current of 1 μA into the sample and by measuring the source to drain voltage drop. With this geometry we were able to measure the conductivity of the sample during the experiment in real time. A Keithley 6517a was used as voltage source and as electrometer to measure the leakage current (being lower than 10 pA) and the induced charge. At each temperature, before and after XAS measurements, the sample resistance and the induced charge have been measured in function of the gate voltage. In Fig. 1 a typical resistance vs. charge polarization curve measured during the experiment, together with the capacitance vs gate voltage characterization, is shown.

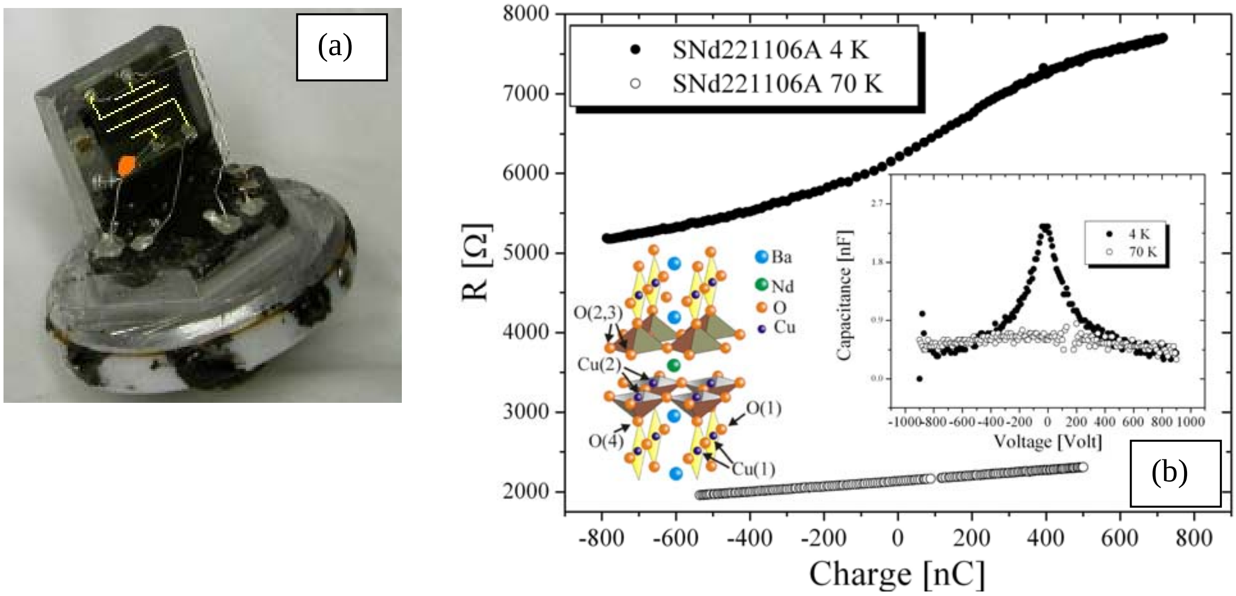

Fig. 1: (a) photo of the modified sample holder used during the XAS experiment;(b) a typical characterization of the device under the application of the electric field: the channel resistance has been measured in fuction of the measured induced charge. In the inset the caracteristiv voltage dependence of thedevice capacitance and a scketch of the NdBCO unit cell with formal assignement of oxygena and Cu inequivalent sites.

The XAS spectra have been collected by disconnecting the electrometer in series between the gate and the sample. This is necessary in order to minimize the noise, since the Total Electron Yield signal is the current that goes from the sample to the ground.

We have studied three FET devices characterized by NdBCO films whose thickness has been carefully tuned in order to modify the transport properties: fully oxygenated 4 u.c. superconducting ((Tc(R=0)=20 K) and 3 u.c. insulating NdBCO, and slightly oxygen depleted insulating 2 u.c. NdBCO (see Tab. 1). Recently we have used X-ray Absorption Spectroscopy (XAS) and Resonant Inelastic X-ray Scattering (RIXS) techniques to investigate the differences on the electronic properties between insulating and superconducting $Nd_{1.2}Ba_{1.8}Cu_3O_7$ (NBCO) epitaxial thin films (experiment HE1737 and ref [1]). Polarization dependent XAS on the Cu $L_{2,3}$ and O K edge of different samples, showed that the thickness induced superconducting-insulating transition is correlated to localization of holes in the out of plane Cu orbital of the charge reservoir layer. In this experiment we measured XAS spectra at the incident angles θ=60°. The V-polarization has always E//ab, while with the H-polarization the electric field forms an angle theta with the c-axis. The measured spectra have been normalized by subtracting a step function. The normalization procedure and any possible incorrect procedure in the data analysis has been verified by performing measurements at temperature higher then 50 K, where the dielectric constant of the STO is much lower and is quasi independent on the electric field. As expected (not shown) the normalized spectra does not show much changes with the application of the electirc field if the temperature is above 70 K, indipendently on the sample conductivity.

Table 1: summary of the characteristics for the samples measured.

SAMPLE	Thickness (unit cells)	Critical Temperature (K)	NOTES
SNd221106B	4	20	Fully oxygenated
SNd221106A	3	Insulating	Fully oxygenated
SNd251106	2	Insulating	Slightly oxygen reduced

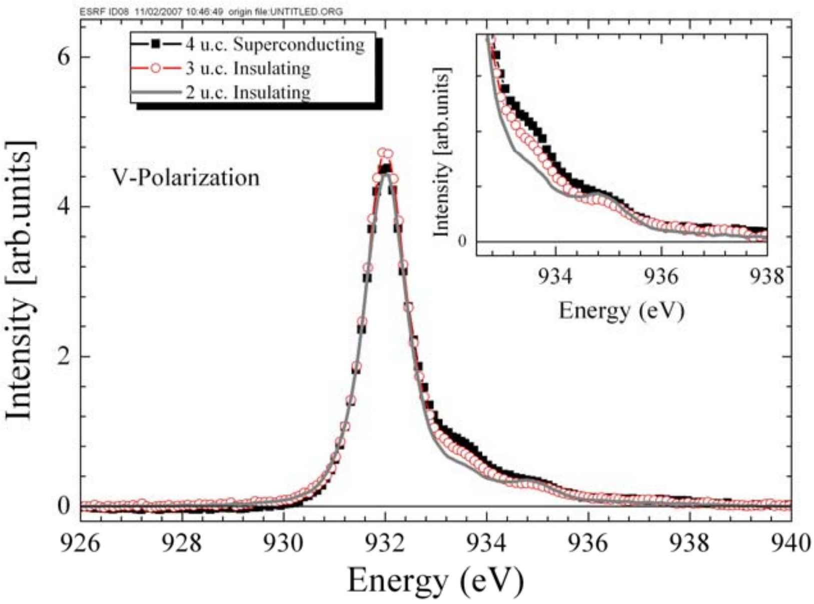

Fig.2: comparison between the V-polarization Cu L_3 XAS spectra on the three investigated samples.

In fig. 2 the Cu L_3 XAS spectra of the 3 FET devices (without application of the electric field) are compared. XAS is composed by essentially three features: 1) a main peak at 932 eV corresponding to excitation of 2p core electron to empty 3d9 orbital with x^2-y^2 symmetry in the case of E//ab and z^2 symmetry for E//c. In NdBCO there are two Cu sites contributing to this peak, one coming from the Cu(2) of the CuO_2 plane, and the other one from Cu(1) in the charge reservoir layer (see inset of Fig.1). This states, together with the 2p O-states, contribute to the Upper Hubbard Band (UHB). A second feature at about 933.4 eV, where the electron is excited to 3d9L ligand empty states, i.e. 3d9 states of copper that are hybridized with O 2p, and in the case of x^2-y^2 orbital form the Zhang-Rice (ZR) singlet. The integrated intensity of this peak is proportional to the number of carriers per CuO_2 plane. Finally a third peak at about 935 eV that is proportional to the number of Cu^{1+} ions, in the Cu(1)O layers.

Similarly to chemical doping, the 3d9L ZR decreases going from 4 u.c. to the 3 u.c. sample. On the other end the 3d9 peak increases because of two effects: a) a transfer of states from the ZR (3d9L) to the UHB band (3d9); b) the localization of holes in the Cu(1)O layer that occurs due to chain-disordering [1]. It is worth noting that the 2 u.c. sample on the other end, is characterized by a higher Cu 3d10 peak and a correspondingly lower 3d9. This result demonstrate that part of 3d9 states in the Cu XAS of NdBCO come from the $Cu(1)^{2+}$ ions, i.e. from Cu in the CR layer, since it decreases substantially switching from the 3 u.c. to the 2 u.c. sample where part of these Cu(1) become monovalent ($Cu(1)^{1+}$) because of oxygen deficiency.

The effect of the electric field on the CuL3 edge is shown in fig. 3 for each sample. The most evident effect is observed on the Cu3d9 peak that, at negative gate voltages (corresponding to hole injection, i.e. positive induced charges), strongly increases for each sample, while the opposite effect is seen for positive gate voltages. A qualitatively similar result is, on the other end, seen also on the 3d9L and 3d10 peaks, that is contrary to what happens with chemical doping. Consequently the weight of unoccupied Cu states is modified by the application of an electric field, and the changes in the orbital occupancies involve not only states contributing to the so called Zhang Rice band, i.e. the “conduction” band associated to the CuO_2 planes, but also to states that are not involved in the conduction and are largely located in the charge reservoir. Note that the strongest changes in the 3d9 peak are observed in the 3 u.c. sample and not in the 2 u.c.. This can be understood by the fact that the Cu(1)O layer of the 2 u.c. sample has a larger number of monovalent Cu(1) and lower number of divalent Cu(2+). Consequently we can attribute electric field induced changes

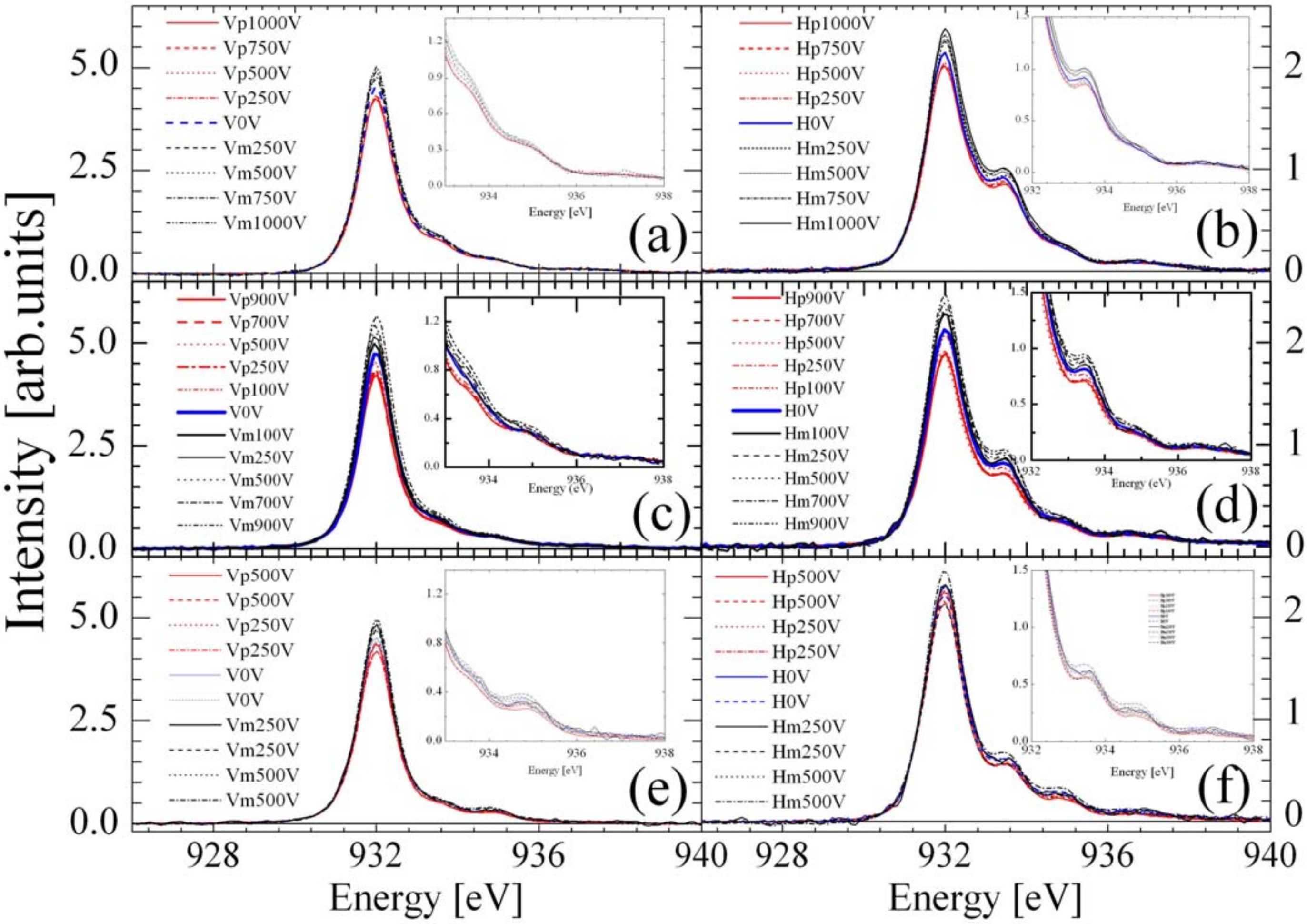

Fig.3: gate voltage dependence of the CuL3 XAS spectra in the 4 u.c. [a) V- polarization and b) H-polarization], 3 u.c. [c) V-polarization and d) H-polarization], 2 u.c. [e) V- polarization and f) H-polarization]. Red lines are for positive gate voltages (hole depletion mode), while black lines are for negative gate voltages (hole accumulation mode), while the blue line is the spectra at zero gate voltage.

occurring into the 3d9 and 3d10 as due essentially to the CR layer. On the contrary the changes in the Cu3d9L in the ab plane involves the number of carriers, and from this moment on we call them "band filling" effects. Note that the electric field not only changes orbital occupanciences in the CuO2 plane, but also out of plane states with dz2 orbital character are modified. Also in the case of H-polarization spectra, we observe strong increase (decrease) of the unoccupied 3d9, 3d9L and 3d10 density of states for negative (positive) gate voltages in the XAS spectra. Consequently part of the induced holes goes in to the out of plane 3d9L that are formed by hybridization of the Cu(2) with the apical oxygen O(4) ions.

It is important to compare the effect of field on the Cu with the XAS on oxygen. Here the analysis is much more complicated because the O-K edge contains many features due to the hybridization of 2p (the final states in the 1s-2p XAS) with Cu and Ba ions, as well as the contribution from the $SrTiO_3$. As shown in Fig. 4a and Fig 4b, the effect of the electric field on oxygen (that has typical 1- or 2- valence) is exactly opposite to that seen on the Cu and Ba, i.e. 2p states are filled (unfilled) by electrons when negative (positive) gate voltages are applied. Since such effect is qualitatively similar on both the 2p final states hybridized with Cu and with Ba, we believe that the oxygen ions, in particular in the CR layer, are polarized due to the effect of the electric field, resulting in an effective change of the density of states of the neighbors atoms. In particular for positive gate voltages we see a filling of the Cu 3d as well as of Ba 4f levels and an emptying of the O 2p levels, i.e. *a decrease of the hybridization between cation-anion orbital, that is a really interesting result.*

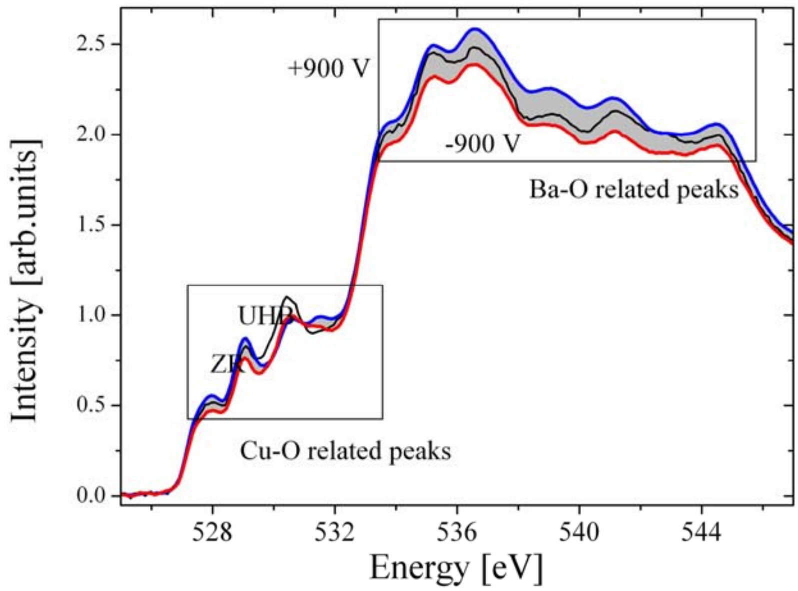

Fig.4: O-K XAS spectra with V-polarization. Blu line is for positive gate voltage, red line is for negatve gate voltage and black line is for zero gate voltage.

Although a more accurate analysis of these findings is needed in order to get a clear picture, a very interesting picture arise from these results. Even by qualitatively analysing the data we can say that a correlation between the difference in the electronics state and transport properties of our thin NBCO films under the application of an electric field can be made. It is worth noting the novelty of our results and of our method that open up new possibilities and feasibility of new class of experiments. From that we can safely state that the experiment was totally successful.

[1] M. Salluzzo, G. Ghiringhelli, N.B. Brookes, G.M. De Luca ,F. Fracassi, and R. Vaglio, *Superconducting-insulator transition driven by out of plane carrier localization in* $Nd_{1.2}Ba_{1.8}Cu_3O_{7+x}$ *ultrathin films,* accepted for publication in **Phys. Rev. B (2007).**