ESRF	**Experiment title:** *Local electronic structure at the Cu sites of ultrathin $Nd_{1.2}Ba_{1.8}Cu_3O_7$ films*	**Experiment number**: HE1737
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Report:

In this experiment we have used resonant inelastic x-ray scattering (RIXS) together with x-ray absorption spectroscopy (XAS) to investigate the local electronic structure of $Nd_{1.2}Ba_{1.8}Cu_3O_{7-\delta}$ (NBCO) films as a fuction of the thickness. Recently we have shown that ultra-thin $Nd_{1.2}Ba_{1.8}Cu_3O_{7-\delta}$ epitaxial films, deposited on STO (100) single crystals, undergo a superconducting-insulating transition when the thickness is reduced to less than 8 unit cells (u.c.). In fig. 1 the transport propertie of 9 and 6 u.c. films are compared, showing the above effect. This system is ideal for such kind of studies, because, due to the strain induced by the STO substrate, NBCO films keep a tetragonal and perfectly in plane matched structure up to very high thickness. Consequently structural changes within the CuO_2 planes are negligible.

Both XAS and RIXS are sensitive to the local properties of the electronic population on an intermediate energy scale (from few hundreds of meV to few eV) and therefore are able to detect even very small changes in the local electronic properties of these samples. Moreover, due to the epitaxial growth of the NBCO films, it has been possible to study the polarization dependence of the RIXS and XAS spectra, which give site-selective information about the Copper and Oxygen electronic density of states. In particular XAS at the Cu $L_{2,3}$ edges and O K edge has been widely used since more than 15 years to probe the anisotropy of the electronic cloud around the Cu sites and to study the hybridisation of Cu 3d states with O 2p states. On the other hand RIXS has shown recently its sensitivity in the study of crystal field excitations (d-d excitations), complementing in this way the information provided by XAS.

In Tab.1 we summarize the characteristics of the investigated samples. In order to understand the properties of thin films, their XAS and RIXS spectra have been compared to the electronic properties of thick superconducting film (optimally oxygenated) and insulating ones obtained by taking out oxygen from Cu(1)O chains.

Table 1: summary of the characteristics for the $Nd_{1.2}Ba_{1.8}Cu_3O_{7-\delta}$ samples measured.

SAMPLE	Thickness (unit cells)	Critical Temperature (K)	NOTES
SNd240705	112	64	Fully oxygenated, $\delta \cong 0$
SNd070605	112	Insulating	Fully oxygen reduced $\delta \cong 1$
SNd150605	9	35	Fully oxygenated $\delta \cong 0$
SNd140605B	6	Insulating	Fully oxygenated $\delta \cong 0$

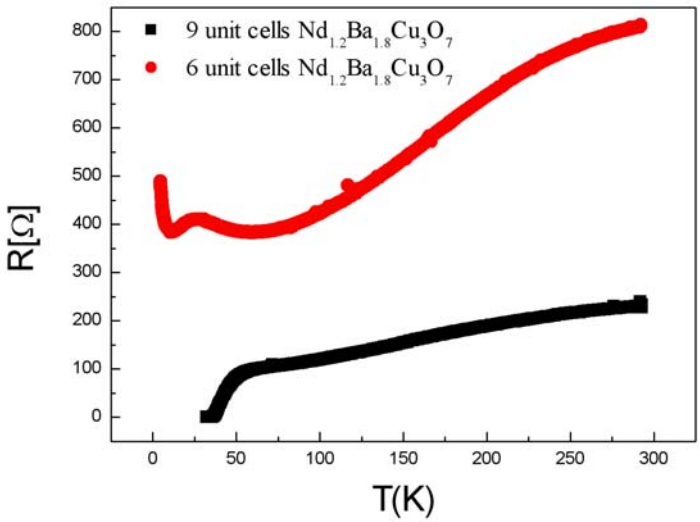

Fig. 1: comparison between the transport properties of 9 and 6 unit cells NBCO films

X-ray Absorption Spectroscopy

For all samples we measured high resolution XAS at the Dragon monochromator of ID08 at the $L_{2,3}$ edges of Cu and at the K edge of O. We used linearly polarised x-rays having the electric vector either vertical (V) or horizontal (H) oriented. The samples had the c-axis (perpendicular to the sample surface) in the horizontal plane and could be rotated around the a-axis: when working at normal incidence the V and H polarization are equivalent, while when working at grazing incidence the V polarisation lies in the ab plane and the H polarisation is perpendicular to the ab plane. In this way it is possible to study the anisotropy of the unoccupied states (holes) associated to Cu and O sites, near to the Fermi level, by simply comparing spectra measured with V and H polarisation at grazing incidence: V polarisation gives peaks in the absorption spectra related to the holes belonging to the ab (CuO_2) planes, H polarisation to those along the c axis. To try to separate spurious effects due to signal saturation, refraction index modulation and surface signal contributions, we have measured the spectra at many incidence angles (85°, 80°, 75°, 70°, 60°, 45° and 0° from the surface normal).

According to dipole selection rules, for *E*//*ab*, only the unoccupied electronic states with O2p_{xy} symmetry are accessible for the O 1*s* transition, and, in the *E*//*c* case, the empty O 2p_z states are probed. Examples of the spectra are shown in fig. 2 and fig. 3 for O and Cu respectively. It is well established that, for the *E*//*ab* spectra in fig. 2 the absorption feature at 528.2 eV in the $RBa_2Cu_3O_7$ cuprates is ascribed to the hole states in the CuO_2 planes, i.e., Zhang-Rice (ZR) states, while the shoulder at 527.6 eV corresponds to the unoccupied states in the Cu(1)O chains [2]. On the other hand the absorption peak at 529.3 eV is related to an Upper Hubbard Band (UHB) with major Cu 3*d* character. At energy higher than 531 eV, especially in the case of the thin films, the spectra may contain contribution from the $SrTiO_3$ substrate, therefore this region has not been further considered in the analysis.

The data taken with E//ab (fig. 2a) show that the holes in the chain and in the CuO_2 planes are markedly reduced in the insulating thick sample when taking out oxygen, in agreement with previous studies. In the case of thin films, however, the situation is different. In the superconducting 9 u.c. sample, compared with the thick superconducting one, we see a reduced intensity of the ZR states with transfer of spectral weight to the UHB band, without a drastic change of the holes in the chains. Therefore there is only a small decrease of the ZR state that is nevertheless in agreement with the reduced T_c and number of carriers. On the contrary the 6 u.c. sample presents a strong decrease of the chain features accompanied by a reduction of the ZR feature and a transfer of spectral weight to the UHB. The 6 u.c. film spectra has some similarity to that of the insulating, oxygen reduced, thick films. However clear differences are seen when analysing the E//c spectra (fig. 2b) where the weight of the peak at 527.6 eV, attributed to the O $2p_z$ unoccupied states, progressively diminishes reducing the thickness, but is well present in the 6 u.c. films while disappear in the oxygen reduced sample. At the same time we see in the thinner samples the appearance of another peak at about 530 eV.

The Cu L_3 XAS spectra (fig.3) show, on the other hand, a prominent $3d^9 \rightarrow 3d^{10}$ peak (930 eV) very sensitive to the photon polarisation.

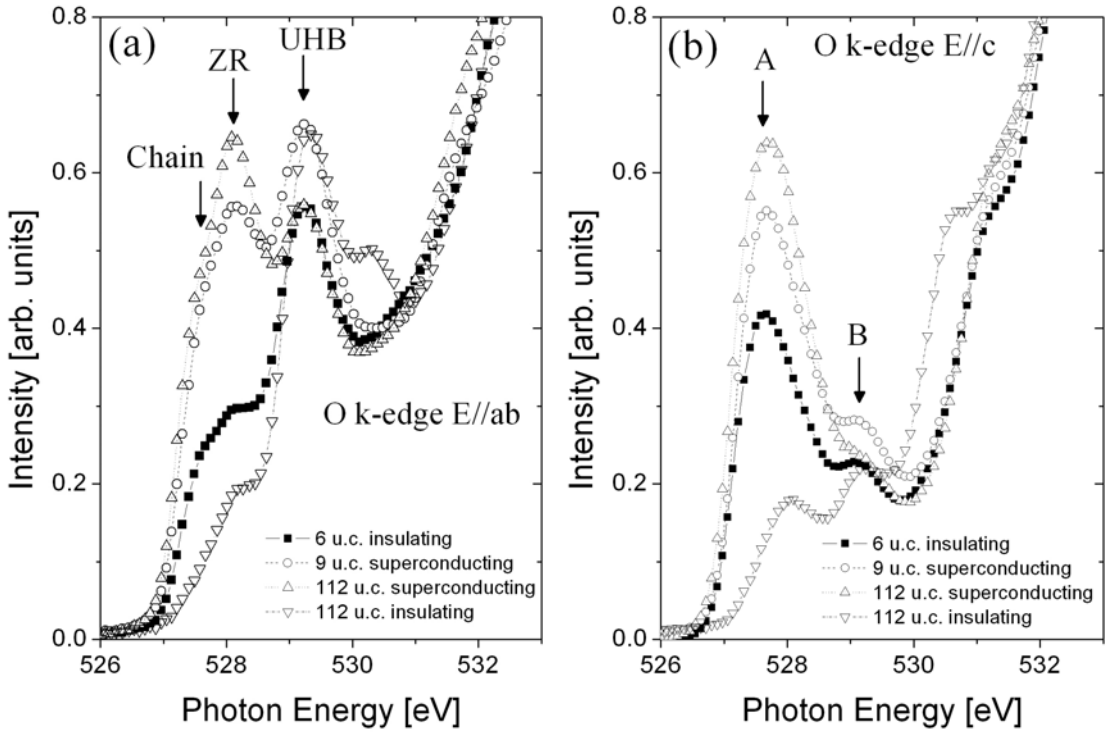

Fig.2: O K-edge XAS spectra of the measured samples listed in Tab.1.
The arrows and labels are explained in the text.

The peak at 932 eV is instead assigned to the "doped sites" in the planes ($3d^9\underline{L} \rightarrow 3d^{10}\underline{L}$ transition, $\underline{L}$ means ligand), where Zhang-Rice singlets are present. It is interesting to notice that this peak is similarly intense in the two thin samples, whereas it disappears in the thick insulating sample. This result confirms that there is only a slightly change of hole doping in the 9 and 6 u.c. samples that is insufficient to explain the marked difference in the transport properties. It must underline that fully oxygenated films present very similar spectra independent on the thickness. In particular while in the oxygen reduced films we observe a peak at 933 eV due to $3d^{10}$ Cu sites (Cu^{1+}) associated to the destruction of Cu(1)O chains, this features is absolutely absent in the other films. This is another very important difference between the 6 u.c and thick insulating samples. In spite of the small difference of the E//ab spectra among the fully oxygenated samples, surprisingly again, we find strong differences when comparing the Cu L_3 spectra with E//c. In particular the ratio between the 932 eV peak (the hole peak) and the 930 eV peak decreases substantially decreasing the film thickness. Moreover the insulating 6 u.c. sample presents a large reduction of the ratio between integrated intensities of the 932 peak and the 930 peak. This data may be interpreted by a progressive localization of holes in the Cu sites of the CuO_2 and Cu(1)O planes, and reduced charge transfer to the apical O(4) site. This feature seems to be correlated with the superconducting-insulating transition. This preliminary result is extremely interesting.

Resonant Inelastic X-ray Scattering

We have measured RIXS spectra, using a 0.65 eV combined energy resolution, on the four samples at 3 excitation energies, using V and H polarisation, at normal and grazing incidence. The 3 excitation energies corresponds to the features described previously indicated by arrows in fig.3a. The analysis of these spectra is more complex as no references to the published literature can be done: this is a very pioneering experiment. Some spectra at grazing incidence are shown in fig. 4a (main peak excitation) and fig. 4b (Zhang-Rice peak excitation).

We see that at the main peak excitation the four samples give very similar spectra: the d-d excitations, that dominate the spectral shape, are indeed very similar when we look at the Cu sites having $3d^9$ populations and lying in the CuO_2 planes. This agrees well with the crystallographic findings stating that little changes occur in the CuO_2 planes when the hole doping is changed. On the other hand when we excite at the Zhang-Rice peak (1.4 eV above the main $3d^9 \rightarrow 3d^{10}$ resonance) the different components in the RIXS spectra

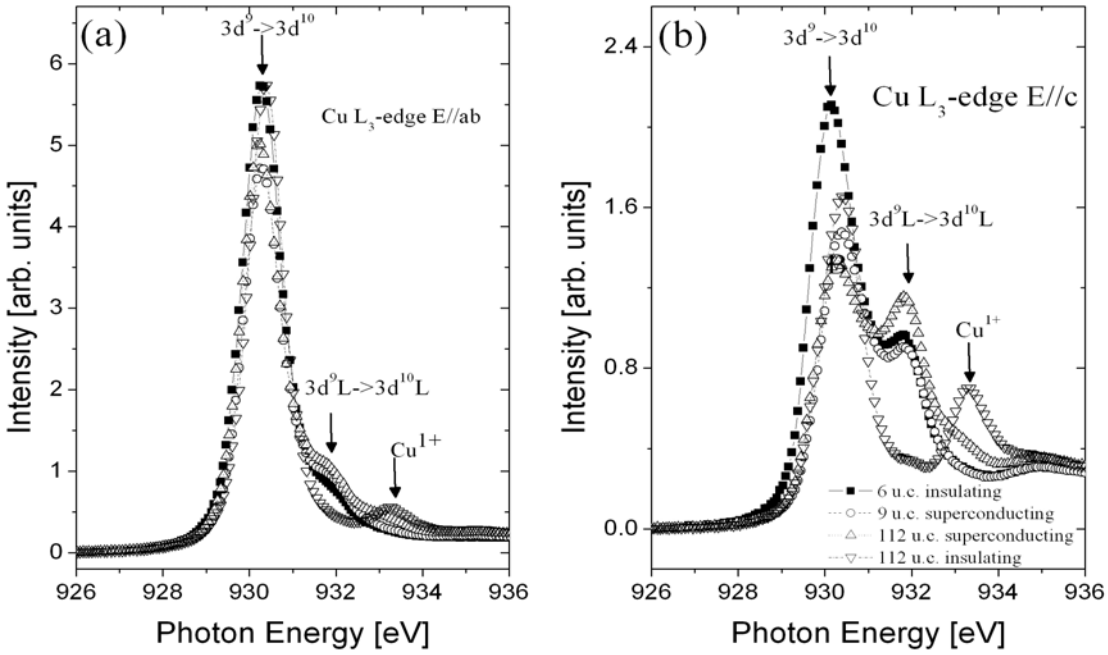

Fig.3: Cu L_3-edge XAS spectra of the measured samples listed in Tab.1.
The arrows and labels are explained in the text.

(around –2 eV and –3 eV) are much more sensitive to the conduction properties of the samples: the thin insulating sample here again gives a spectrum somehow similar to the thick insulating sample!

A very interesting picture arises from these results. However a more accurate analysis of these findings is needed in order to get a clear interpretation of the results. Nevertheless 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 can be made. From that we can safely state that the experiment was totally successful.

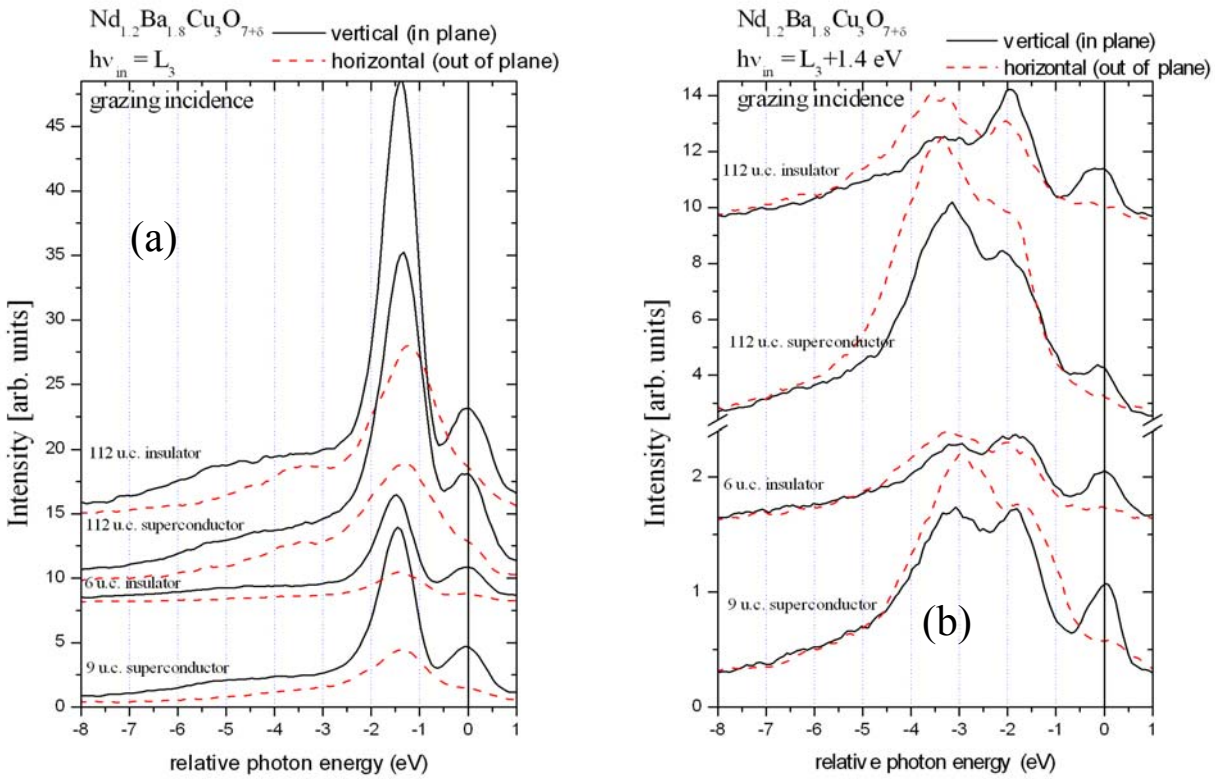

Fig. 4: RIXS spectra of the NdBCO samples listes in Tab. 1 taken at grazing incidence
at the L3 and L3+1.4 eV excitation energy for vertical (black) and horizontal (red). polarizations.