

# X-ray Fluorescence Spectroscopy of $\text{GdBa}_2\text{Cu}_3\text{O}_x$ Thin Films.

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Oxygen content is a prominent factor controlling superconducting behavior of Cu oxide superconductors; in fact both the normal state electrical properties and superconductivity of  $\text{MBa}_2\text{Cu}_3\text{O}_x$  ( $6 \leq x \leq 7$ ) compounds (M=Y or rare earths excluding Ce and Tb) depend strongly on oxygen content.

For bulk samples, there is a consistent body of literature linking the O deficiency in 123 compounds to some of the basic properties of high  $T_c$  superconductors. In particular the critical temperature  $T_c$  is known to depend strongly on the hole carrier density which can be varied by charge compensation or oxygen non-stoichiometry.

In thin films, however, some of these parameters become variable depending on the sample preparation technique and growth conditions. In particular, due to the variable copper valence, the equilibrium oxygen content can be varied continuously ( $6 \leq x \leq 7$ ) in the thin films as a function of substrate temperature and oxygen partial pressure. This fact, together with the peculiar morphology of the films enables researchers to obtain important information on the structure and superconducting behavior of the material under examination.

However, effects of oxygen non-stoichiometry on electronic properties of thin films are not well known and comparisons with the same properties on bulk samples have not been reported.

This field has benefited greatly from spectroscopies such as photoemission and x-ray fluorescence spectroscopy (XES) [1,2,3,4]. The latter technique has the advantage of being less surface sensitive and so can be used to study bulk properties, and elaborate preparation is not necessary.

The samples available were  $\text{GdBa}_2\text{Cu}_3\text{O}_x$  oxygen deficient films ( $6.3 < x < 6.8$ ) deposited on (110) oriented  $\text{NdGaO}_3$ . These have been prepared ex situ by controlled annealing under reduced oxygen pressure at  $400^\circ\text{C}$ . Films had thicknesses from 40 to 200 Angstroms and stacking fault densities about 0.5%, i.e. perfectly crystalline as far as this spectroscopy is concerned.[5,6]

To clarify the role and contribution to the superconducting behavior of inequivalent oxygen sites we have done XES and XAS measurements at beamline 8.0.1 and tried to have an identification of the absorption and emission lineshape in terms of different oxygen atoms and sites, the induced hole distributions and overall experimental and theoretical pDOS as a function of oxygen content of the samples.

We selectively excited the variable oxygen content films in the energy range needed to obtain absorption (total fluorescence yield mode) and emission spectra above, below and at the resonance for O K and Cu L edges and local partial density of states in the VB was experimentally obtained.

The valence band of high-T<sub>c</sub> superconductors of perovskite type is known to be formed mostly by Cu-3d and O-2p states. X-ray emission Cu-L (3d to 2p transition) and O-K (2p to 1s transition) spectra arise from dipole allowed transitions from the valence band to inner shell vacancies. The experimental study of the electronic partial density of states is therefore facilitated in this case by the fact that the fluorescence spectra are well separated in energy.

Multiplet effects in emission and absorption measurements at the L<sub>2,3</sub> edge of 3d transition metals can significantly modify the edges from their single particle interpretation. The origins of these modifications are extremely important in correlated systems since they are a direct consequence of correlations between the 2p and 3d core holes and within the 3d band.

Absorption and emission measurements have therefore been done at the Cu L<sub>2,3</sub> edge in the hope to pinpoint significant differences and analogies with theoretical one electron type calculations.

A problem met in the investigation is that the obtained data are quite sensitive to the quality of the samples. In particular, there is an overlapping of the Cu L edge spectra with spurious signal coming from the substrate.

A high sensitivity to the quality of the samples was to be expected in the case of thin films and is also reported in literature.

In the O 1s absorption spectra a peak is present in the pre-edge region which is strictly related to the oxygen content of the sample and can be associated with the unoccupied O 2p states. The peak shifts in energy and changes in intensity in different samples according to O content. In O rich samples holes are formed upon p-type doping and the pre-edge peak shifts close to the Fermi edge with possible formation of states in the gap. [Fig.1]

In the O XES spectra, different O chemical environments will determine different emission energy values for transitions to core 1s states (2p-1s transitions). The chemical shift can be exploited to selectively excite different site O contributions. Experimental results show a shift both in the low energy shoulder and in the peak maximum energy value for different O content of the samples. [Fig2]

## REFERENCES

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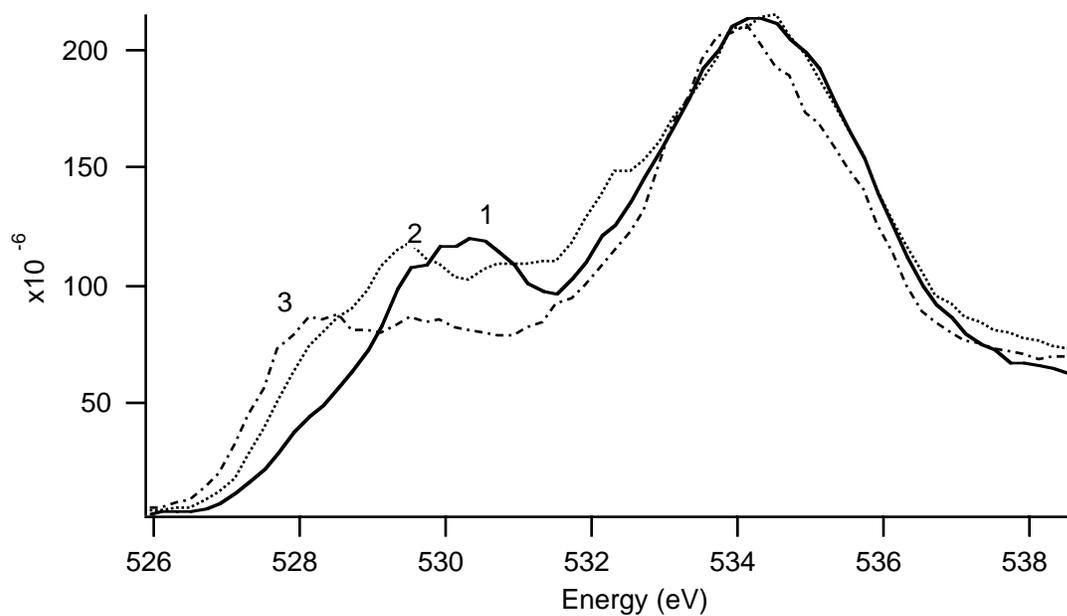


Figure 1. O 1s X-ray absorption spectra taken in total fluorescence yield mode. 1)  $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5-\delta}$  2)  $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$  3)  $\text{GdBa}_2\text{Cu}_3\text{O}_{6.8}$

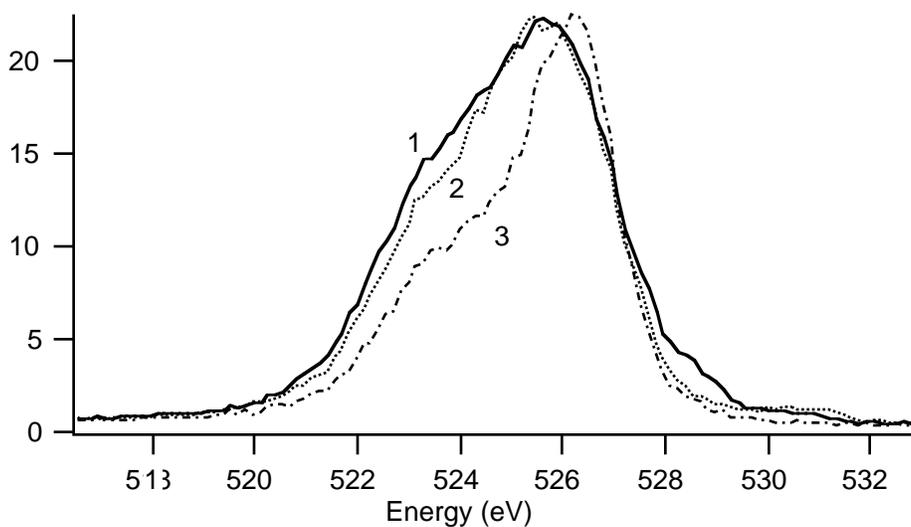


Figure 2. O  $K\alpha$  X-ray emission spectra taken at the prepeak maximum values of the absorption spectra for the respective samples. 1)  $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5-\delta}$  2)  $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$  3)  $\text{GdBa}_2\text{Cu}_3\text{O}_{6.8}$

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