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STUDIES OF Y-Ba-Cu-O SINGLE CRYSTALS BY X-RAY ABSORPTION SPECTROSCOPY*

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ABSTRACT

The symmetry and density of unoccupied states of $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ have been investigated by orientation dependent x-ray absorption spectroscopy on the O 1s edge using a bulk-sensitive fluorescence-yield-detection method. It has been found that the O 2p holes are distributed equally between the CuO_2 planes and CuO chains and that the partial

density of unoccupied O 2p states in the CuO_2 planes are identical in both systems investigated. The upper Hubbard band has been observed in the planes but not in the chains in both systems.

INTRODUCTION

Orientation dependent x-ray absorption spectroscopy (XAS) at the O 1s edge is a useful tool to measure the partial unoccupied DOS and its symmetry at the O sites. This method was applied to the $YBa_2Cu_3O_7$ (Y123) and $YBa_2Cu_4O_8$ (Y124) superconductors. In these systems besides the CuO_2 planes formed by Cu(2) and O(2,3) atoms there are also chains along the *b*-direction formed by Cu(1), O(1), and the apex O(4) atoms. In Y124 there is an additional CuO chain in antiregister with the chain which exists in Y123. As a result the O(1) atoms in Y124 are coordinated with 3 Cu(1) atoms while in Y123 they are coordinated only with 2 Cu(1) atoms. The holes are formed upon doping the respective parent compound with the additional O(1) atom which oxidizes the Cu(1) atom from Cu^+ to Cu^{++} and therefore contributes more positive charge. Created holes are shared by the CuO_2 planes and the CuO chains. The goal of this work was to obtain information on the ratio of the number of holes in planes and that in chains. This problem has been studied in a previous investigation of orientation-dependent O 1s absorption edges of twinned Y123 single crystals using EELS[1] in transmission. The EELS experiments gave evidence for about two times as much holes in O $2p_{x,y}$ orbitals compared to those in O $2p_z$ orbitals. However twinning present in these crystals hindered reliable evaluation of the O 2p distribution between the CuO chains and the CuO_2 planes.

EXPERIMENTAL

Single crystals of Y123 were grown in a ZrO_2 crucible and oxidized to show a sharp superconducting transition at 91 K. They were heated in flowing oxygen to 400 °C and subjected to uniaxial stress while slowly cooling them down to form twin free samples.[2] The Y124 single crystals were grown[3] using high oxygen pressure (2.7 Kbar) at 1170 °C; the measured T_c was 80 K. Y123 and Y124 crystals were glued to the sample holder using silver paint and oriented to permit measurements with the E vector of the x-rays parallel to the *a*-axis and to the *b*-axis. They were then mounted in a vacuum chamber near the soft-x-ray fluorescence detector. The soft-x-ray absorption at the O 1s edge was measured at the AT&T Bell Laboratories Dragon high resolution beam line at the NSLS at Brookhaven National Laboratory.[4] During the experiment, the monochromator resolution was set at 250 meV. The oxygen K_α fluorescence yield was monitored by means of a low pressure parallel plate avalanche chamber.[5] All measurements were performed in an energy range $520 \leq \hbar\omega \leq 570$ eV. The spectra were normalized to the integrated area between 534 and 560 eV after subtracting an energy-independent background.

RESULTS

In Fig. 1 we show a typical O 1s absorption spectrum of a *c*-axis oriented Y123 film on YSZ substrate obtained by laser ablation.[6] The E vector was parallel to the CuO_2 plane.

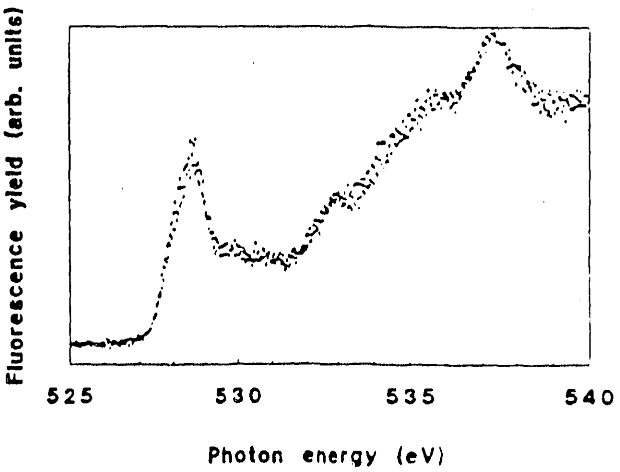

Fig. 1. Half of the sum of the O 1s absorption spectrum for $E//a$ and $E//b$ (triangles) compared to a spectrum of a *c*-axis oriented $YBa_2Cu_3O_7$ prepared by laser ablation (crosses).

According to previous measurements the first peak at 528.8 eV is due to hole states formed upon doping. The rise in spectral weight above 531 eV is due to Ba 5d and Y 4d states hybridized with O 2p states. In Fig. 1 we also show a second O 1s spectrum which is composed of spectra obtained with untwinned Y123 crystals for *E//a* and *E//b*. The perfect agreement of the two spectra shown in Fig. 1 demonstrates the reliability of our data and normalization procedure used.

In Fig. 2 we show the O 1s edges in the pre-edge region (527-531 eV) for Y123 and Y124 as measured for *E//a* and *E//b* together with the difference spectra between the two directions (*E//b* – *E//a*).

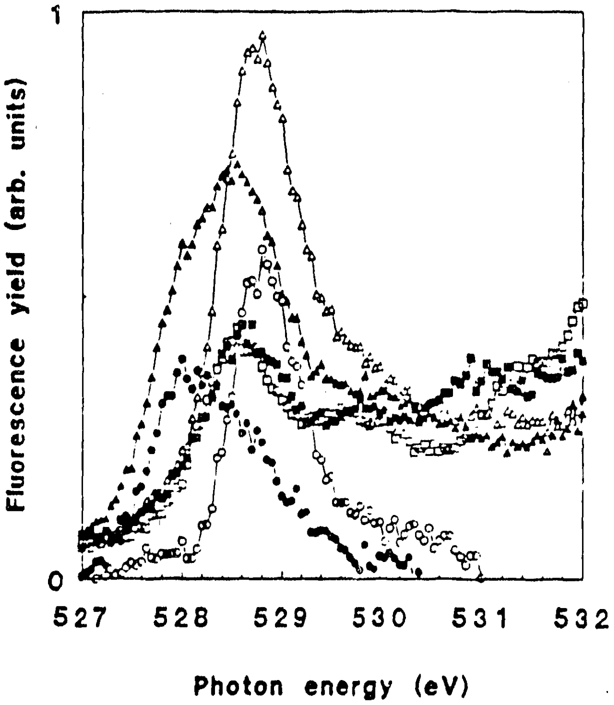

Fig. 2. O 1s x-ray absorption spectra for $YBa_2Cu_3O_7$ *E//a:* filled squares, *E//b:* filled triangles, difference spectrum (*E//b* – *E//a*): filled circles, and $YBa_2Cu_4O_8$ *E//a:* open squares, *E//b:* open triangles, difference spectrum (*E//b* – *E//a*): open circles.

For *E//a* the absorption edges for Y123 and Y124 as measured are almost identical with two maxima at 528.6 and 529.7 eV; however, the threshold observed in Y124 is slightly shifted towards higher energy as compared with Y123. For ***E//b*** the spectral weight near 528.6 eV is almost twice as high as for ***E//a***. The pre-edge peak of the difference spectrum (***E//b*** – ***E//a***) is slightly shifted to lower energies as compared to the spectrum ***E//a***, while for Y124 the opposite shift is observed.

In order to understand these spectra it is necessary to consider the orbital character of the unoccupied states as derived from band structure calculations.[7-12] According to these calculations the unoccupied partial density of states on O sites near the Fermi level E_F in Y123 and Y124 is predominantly caused by holes in orbitals which are σ-bonded to Cu atoms. In Y123 there is an additional contribution from a narrow dpπ band formed by O(1,4) and Cu(1) atoms. Since the Fermi level is right at the top of this band, the contribution to the total unoccupied DOS is small although it contributes considerably to the density of states at E_F. In Y124 this band is completely filled and no contributions from π-bonded O2p orbitals are expected for the unoccupied DOS. Therefore, according to band structure calculations the unoccupied partial DOS at O sites is predominantly formed in O orbitals σ-bonded to Cu atoms.

Based on this result, the XAS spectrum for ***E//a*** is mainly due to O(2) atoms and that for ***E//b*** is caused by O(3) and O(1) atoms. The difference spectrum is caused *solely* by O(1) atoms when assuming an isotropic hole-distribution in the planes. In Y123 the experimental O 1s binding energies as determined from the absorption edge of O(1) and O(4)[14] are found to be smaller by 0.4 and 0.7 eV, respectively, when compared to those of O(2,3) atoms. This is in the range of calculated values.[15,16,18] In Y124 the observed O 1s binding energies of the O(2) and O(3) atoms are the same within 0.1 eV and the O 1s binding energy of the O(1) is about 1.1 eV larger than in Y123. As it was mentioned before this latter finding can be explained by the fact that in Y124 the O(1) atom is coordinated with three Cu atoms while in Y123 there are only two nearest-neighbor Cu atoms. The large shift ($\sim$ 3 eV) of the threshold for the unoccupied DOS at the O(1) atoms in Y124 to higher energies was predicted by the band structure calculations in the LDA approximation.[13] These calculations gave rise to the similar O 2p hole DOS at the O(2,3) atoms in both the investigated structures.

The second peak at ~530 eV is observed for ***E*//*a*** and ***E*//*b*** polarization in Y123 and Y124. Zaanen et al.[10] proposed that this feature was due to van Hove singularity of the top of (1D) chain band probed by the O(1) $2p_y$ states. However, the mere fact that we observed this peak for ***E*//*a*** rules out this explanation since transition to the chain band are for this orientation dipole-forbidden. In previous investigations[14] this peak has been observed in $YBa_2Cu_3O_6$ as well. According to recent studies[15,16] on $La_{2-x}Sr_xCuO_4$, this peak can be ascribed to transitions into the conduction band (upper Hubbard band) which is predominantly formed by Cu 3d states but has some admixture of O 2p states. At higher dopant concentration, this peak is reduced due to a reduction of correlation effects and due to hybridization of the valence and the conduction band in the final state.[17] It is interesting to note that this second peak is not observed for O(1) in the difference spectrum ***E*//*b*** – ***E*//*a*** nor for O(4) in the EELS spectra.[18] We tentatively interpret the absence of the conduction band peak in the chains in terms of a stronger Cu-O hybridization in the chains compared to that in the planes which was derived from band structure calculations as well.[11] However, it might also be possible that the charge transfer gap is smaller for the Cu-O chains as compared to that for the CuO_2 planes.

From the experimental ratios for the in-plane and out-of-plane absorption $I_{a,b}/I_c = 2.0$ (2.6) measured by EELS on twinned samples and the present XAS result $I_b/I_a = 2.0$ (2.0) on untwinned crystals for Y123 (Y124) one can easily calculate the partial hole concentration on different sites when taking the sum of the holes to be one. The evaluation gives nearly the same hole concentration at O(2), O(3) and O(4) atoms in Y123 and Y124 . The holes present on O(1) sites in Y123 are found to be evenly distributed between two O(1) sites in Y124. It is interesting to note the equidistribution of the O 2p holes between chains and planes in both investigated systems.

CONCLUSIONS

In summary, from orientation-dependent O 1s XAS spectra of twin-free Y123 and Y124 single crystals together with a previous EELS study, it has been found that the O 2p holes are distributed equally between the CuO_2 planes and CuO chains and that the partial density of unoccupied O 2p states in the CuO_2 planes are almost identical in both investigated systems. The measured unoccupied DOS in the chain is different in Y123 and Y124. The upper Hubbard band is observed in planes but not in chains in both systems.

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