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Hole states in CuO_2 planes and Cu-O chains of $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ probed by soft-x-ray absorption spectroscopy

A. Krol, Z. H. Ming, and Y. H. Kao
Department of Physics, State University of New York at Buffalo, New York 14260

N. Nücker, G. Roth, and J. Fink
Institut für Nukleare Festkörperphysik, Kernforschungszentrum Karlsruhe,
Postfach 3640, W-7500 Karlsruhe, Federal Republic of Germany

G. C. Smith
Brookhaven National Laboratory, Upton, New York 11973

Key Taeck Park, Jaejun Yu, and A. J. Freeman
Department of Physics, Northwestern University, Evanston, Illinois 60208

A. Erband and G. Müller-Vogt
Institut für Kristallchemie, Universität Karlsruhe, W-7500 Karlsruhe, Federal Republic of Germany

J. Karpinski and E. Kaldis
Labor für Festkörperphysik, Eidgenössiische Technische Hochschule Zürich, Hönggerberg, CH 8093 Zürich, Switzerland

K. Schönmann
Walter-Meissner-Institut, W-8046 Garching, Federal Republic of Germany

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The symmetry and density of unoccupied states of twin-free $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ single crystals have been investigated by orientation-dependent x-ray absorption spectroscopy at the O 1*s* edge, using a bulk-sensitive fluorescence-yield-detection method. In conjunction with earlier results obtained by electron-energy-loss spectroscopy, the relative density of unoccupied states for different oxygen sites has been derived. Comparison with local-density energy-band-structure calculations shows reasonable agreement with the experimental results.

Common to all cuprate high-T_c superconductors (HTSC) are *p*-type or *n*-type doped CuO_2 planes which are believed to be responsible for superconductivity. Doping is established by neighboring structures. The undoped parent compounds are antiferromagnetic insulators with a charge-transfer gap induced by on-site Coulomb interactions at the Cu sites. This is in contrast to what is derived from standard band-structure calculations in the local-density approximation (LDA) where a metallic state is predicted. In addition to the study of the band structure $E(k)$, the investigation of partial density of states (DOS) close to the Fermi level is also important for the understanding of these correlated compounds. These experiments are essential for testing the validity of model calculations.

Orientation-dependent x-ray-absorption spectroscopy (XAS) and electron-energy-loss spectroscopy (EELS) offer the possibility of measuring the partial unoccupied DOS and its symmetry at the O and Cu sites provided that core-hole effects are negligible. Experiments of this kind on HTSCs have been performed on single crystals of $Bi_2Sr_2CaCu_2O_{8+x}$. There, it was realized[1,2] that the hole states on O sites created upon doping are formed in O $2p_{x,y}$ and not in O $2p_z$ orbitals.

The situation is more complicated in the system $YBa_2Cu_3O_{7-\delta}$ (Y 1:2:3) where, 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. Starting from $YBa_2Cu_3O_6$ the additional O(1) atom in Y 1:2:3 oxidizes the Cu(1) atom from Cu^+ to Cu^{2+} and a further positive charge forms a hole which is shared by the CuO_2 planes and the CuO chains. It is interesting to obtain information on the ratio of the number of holes in planes to that in chains. A previous investigation[1] of orientation-dependent O 1*s* absorption edges of twinned Y 1:2:3 single crystals using EELS (Ref. 2) in transmission gave evidence for about twice as many holes in O $2p_{x,y}$ orbitals compared to those in O $2p_z$ orbitals. From a comparison of the absorption thresholds with calculations of O 1*s* binding energies of the four individual O atoms the O $2p_z$ states were assigned to holes in O(4) 2*p* orbitals while the O $2p_{x,y}$ states correspond to hole states in 2*p* orbitals in O(2) and O(3) atoms in the CuO_2 planes and in O(1) atoms in the chains. This implies a σ bonding of holes to Cu sites in agreement with NMR measurements.[3,4]

In the present paper we report on the results of first measurements on *twin-free Y 1:2:3 single crystals* using XAS in the fluorescence detection mode. These crystals offer the possibility of performing measurements with polarization along and perpendicular to the chain direction. Therefore, more information on the distribution of holes between planes and chains is obtained. The experimental results are compared to calculations of the unoccupied density of states in the framework of LDA band-structure calculations.

Single crystals of Y 1:2:3 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 down to form twin-free samples.[5] The Y 1:2:4 single crystals were grown[6] using high oxygen pressure (2.7 kbar) at 1170 °C. Y 1:2:3 and Y 1:2:4 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 the 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.[7] 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.[8] All measurements were performed in an energy range $520 \leq \hbar\omega \leq 570$ eV. The spectra were normalized to the integrated intensity between 534 and 560 eV after subtracting an energy-independent background.

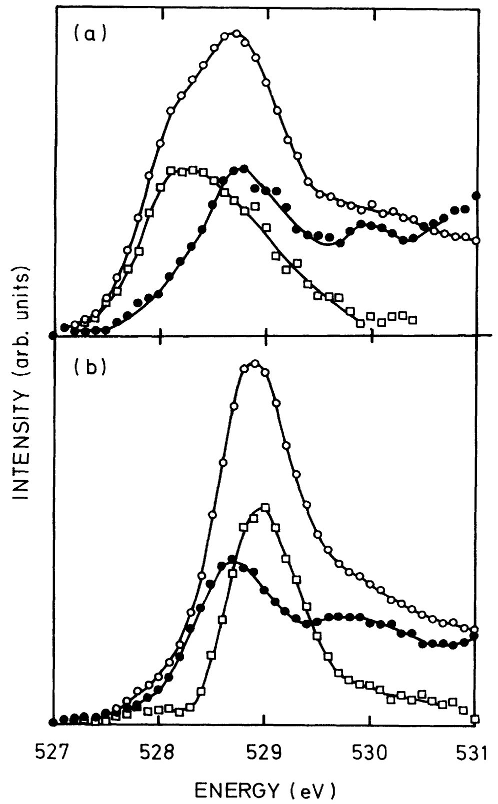

FIG. 1. O 1s x-ray-absorption spectra for (a) $YBa_2Cu_3O_7$ and (b) $YBa_2Cu_4O_8$. $E \parallel a$, solid circles; $E \parallel b$, open circles; difference spectrum ($E \parallel b - E \parallel a$), squares.

In Fig. 1 we show the O 1s edges in the pre-edge region (527–531 eV) for Y 1:2:3 and Y 1:2:4 as measured for $E \parallel a$ and $E \parallel b$ together with difference spectra between the two directions ($E \parallel b - E \parallel a$). For $E \parallel a$ the absorption edges for Y 1:2:3 and Y 1:2:4 as measured are almost identical with two maxima at 528.6 and 529.7 eV. However, the threshold observed in Y 1:2:4 is slightly (~0.3 eV) shifted towards higher energy as compared with Y 1:2:3. For $E \parallel b$ the spectral weight near 528.6 eV is almost twice as high as for $E \parallel a$. The prepeak of the difference spectrum ($E \parallel b - E \parallel a$) is slightly shifted to lower energies as compared to the spectrum $E \parallel a$, while for Y 1:2:4 the opposite shift is observed.

In Fig. 2, we show calculated spectra of O 1s absorption edges for $E \parallel a$, $E \parallel b$, and the difference spectra $E \parallel b - E \parallel a$ as given by

$$I_{a,b}(\epsilon) \propto \sum_i \int N^i_{a,b}(\epsilon_{2p})\,\delta[\epsilon - \epsilon_{2p} + E_{1s}(i)]\,d\epsilon_{2p}\,, \tag{1}$$

where summation i goes over individual O sites. The partial O 2p DOS, $N^i_{a,b}(\epsilon_{2p})$, at the ith O site is calculated by using LDA band-structure results and projected onto the a and b axis, respectively, in accordance with its orbital character. Also calculated are the O 1s core levels (i.e., chemical shifts) of each O site. The absolute scales in Fig. 2 are determined for Y 1:2:3 and Y 1:2:4 from the LDA band-structure calculations. Further, the calculated spectra have been broadened by a Gaussian with a full width at half maximum of 0.3 eV. The calculated spectra for $E \parallel a$ are almost identical for Y 1:2:3 and Y 1:2:4 showing a prepeak about 2 eV wide with a total spectral weight of ~0.8 states. For $E \parallel b$ in Y 1:2:3, the prepeak is about a factor of 2 higher and has a similar shape. For $E \parallel b$ in Y

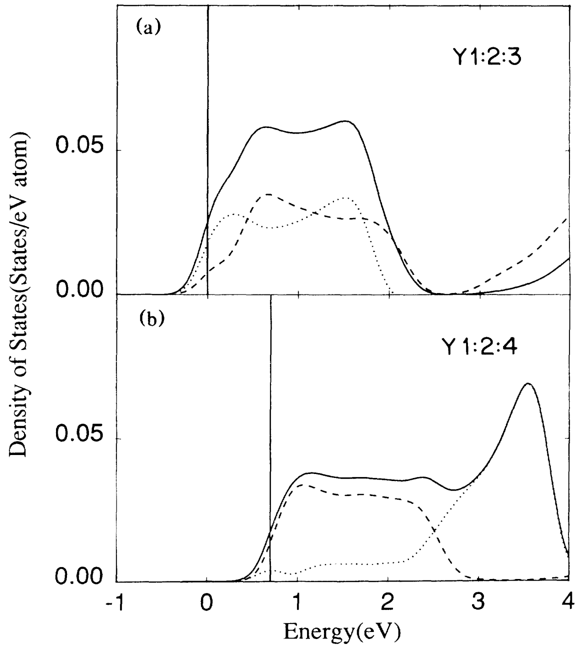

FIG. 2. Results of LDA band-structure calculations for (a) $YBa_2Cu_3O_7$ and (b) $YBa_2Cu_4O_8$. $E \parallel a$, dashed line; $E \parallel b$, solid line; difference spectrum ($E \parallel b - E \parallel a$), dotted line.

1:2:4 the situation is quite different. Close to the threshold there is almost no spectral weight in the $E \parallel b - E \parallel a$ difference spectrum, but 3 eV above the threshold there is a pronounced peak. In this case the total spectral weight of the prepeak is ~1.8 states. According to band-structure calculations,[9–14] the unoccupied partial density of states on O sites near the Fermi level E_f in Y 1:2:3 and Y 1:2:4 is predominantly caused by holes in orbitals which are σ bonded to Cu. In Y 1:2:3 there is an additional contribution from a narrow $dp\pi$ 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 Y 1:2:4, this band is completely filled and no contributions from π-bonded O $2p$ 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.

Based on this result, the XAS spectrum for $E \parallel a$ is due to O(2) atoms, while that for $E \parallel b$ is caused by O(3) and O(1) atoms. The difference spectrum is caused by O(1) atoms assuming an isotropic hole distribution in the planes. In Y 1:2:3, the experimental O $1s$ binding energies as determined from the absorption edge of O(1) and O(4) are found to be smaller by 0.4 and 0.7 eV, respectively, when compared to those of O(2,3) atoms. This is within the range of calculated values.[12,13,15,16] The experimental data show the same O $1s$ binding energies for O(2,3,4) atoms within 0.1 eV for Y 1:2:3 and Y 1:2:4 and a shift ~0.8 eV for O(1) atoms in Y 1:2:4 as compared to the O $1s$ binding energy of the O(1) in Y 1:2:3. The larger shift of the O(1) core levels in Y 1:2:4 relative to that in Y 1:2:3 was predicted (Ref. 13 in the text) and estimated to be ~2 eV, which is now compared to the experimental value of the O(1) binding energy shift ~0.8 eV, where such a large shift of the O(1) was attributed to a change of the Madelung potential at the O(1) site. This can be explained by the fact that in Y 1:2:4, the O(1) atom is coordinated with three Cu atoms while in Y 1:2:3 there are only two next-nearest Cu atoms. Thus there is a shift of the threshold for the unoccupied DOS at the O(1) atoms to higher energies, causing the peak at 3 eV above threshold in Fig. 2(b). We emphasize, however, that there is a considerable spread among the calculated O $1s$ binding energies[12,13,15,16] and therefore there may be differences when compared with experimental results.

In the following, we interpret the experimental data shown in Fig. 1 in terms of holes in O $2p$ orbitals which are σ bonded to Cu, as predicted by the band-structure calculations. This is supported by the EELS result and by the NMR experiments,[3,4] and by a calculation of electrical-field gradients together with a comparison with NMR experiments.[17] In addition, we assume that the O $1s \rightarrow 2p$ transition probability for the individual O sites is roughly the same. Finally, the EELS investigations[2,18] are taken into account in which the relative O $1s$ absorption strength and O $2p_{x,y}$ and O $2p_z$ orbitals have been determined. Then, from the measured intensities, the number of hole states on the different O sites formed upon doping can be derived.

The prepeak intensity of the measured spectrum for $E \parallel a$ is due to O(2) atoms in the plane. That of the difference spectrum $E \parallel b - E \parallel a$ is due to O(1) and that in the EELS spectra for momentum transfer $q \parallel c$ is due to O(4) atoms. From the experimental ratios for the in-plane (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 Y 1:2:3 (Y 1:2:4), one can easily calculate the hole concentration on the different sites when taking the sum of the holes to be one. The result is shown in Table I together with values derived from the band-structure calculations[11] and values derived from a comparison of electrical-field gradient calculations with NMR experiments.[17] The evaluation gives nearly the same hole concentration for Y 1:2:3 and Y 1:2:4 for O(2), O(3), and O(4) atoms. The same number of holes on O(1) sites in Y 1:2:3 are found to be distributed to two O(1) sites in Y 1:2:4. The calculated values show significant deviations from the present results. In particular, we note for Y 1:2:3 the much smaller hole number on O(1) sites derived from band-structure calculations. The NMR calculations are in better agreement with the XAS/EELS results.

It is also interesting to compare the present results with orientation-dependent studies of the plasma edge in Y 1:2:3 measured by optical reflectivity.[19,20] If we neglect a possibly different background dielectric function near the plasma frequency, assume the same effective mass for chains and planes, and use a simple Drude model, we may derive from the plasmon edges for $E \parallel a$ and $E \parallel b$ the ratio of holes $n(b)/n(a) = 2.35$. This value is quite close to the a,b anisotropy observed in O $1s$ XAS spectra.

Above the first prepeak, a further peak about 1.5 eV above the threshold is seen in the spectra $E \parallel a$ for Y 1:2:3 and Y 1:2:4. In previous investigations,[2] this peak was observed in YBa$_2$Cu$_3$O$_6$ as well. According to recent studies[21–23] on La$_{2-x}$Sr$_x$CuO$_4$, this peak can be ascribed to

TABLE I. Distribution of holes to different oxygen sites obtained from a combination of XAS/EELS experiments. Values from band-structure calculations (Ref. 11) (BSC) and electric-field gradient (Ref. 17) (EFG) calculations are shown for comparison.

		YBa$_2$Cu$_3$O$_7$			YBa$_2$Cu$_4$O$_8$	
Site	atoms/unit	XAS/EELS	BSC	EFG	atoms/unit	XAS/EELS
O(1)	1	0.27	0.17	0.30	2	0.13
O(2)	2	0.13	0.14	0.12	2	0.13
O(3)	2	0.13	0.16	0.13	2	0.13
O(4)	2	0.10	0.10	0.14	2	0.10

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 diminished because of a reduction in correlation effects and because of hydridization of the valence and conduction band in the final state.[24] It is interesting to note that this second peak is only detected in the $E \| a$ spectra, which are due to O(2) and O(3) atoms, while it 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 produced by the chains in terms of a stronger Cu-O hybridization in the chains compared to that in the planes. Stronger Cu-O hybridization in the chains has also been derived from band-structure calculations.[13]

In summary, from orientation-dependent O 1s XAS spectra of twin-free Y 1:2:3 and Y 1:2:4 single crystals, together with a previous EELS study, the number of holes on the four individual O sites has been determined. There is reasonable agreement with results derived from band-structure calculations.

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