Electronic structure of high-T_c superconductors from soft-x-ray absorption

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A series of high-T_c superconductors was studied using soft x-ray absorption spectroscopy at the Cu-$L_{\text{II,III}}$ thresholds. From a comparison with CuO and $NaCuO_2$, it is shown that these superconductors contain mostly $3d^9$ and $3d^9\underline{L}$ ($\underline{L}$=oxygen ligand hole) configurations in the ground state, with negligible amounts of Cu(III) $3d^8$. The spectral weights of the $3d^9\underline{L}$ components are found to be higher for the $YBa_2Cu_3O_7$-type superconductors than for the La_2CuO_4-derived compounds and exceed the values expected from oxygen stoichiometry.

Ever since the discovery of high-T_c superconductivity in copper-based oxides,[1] there has been intensive activity to further increase T_c.[2,3] Paralleling this search for higher T_c, numerous theoretical efforts to understand the mechanism of superconductivity in these compounds have been undertaken.[4] From simple charge balance arguments, assuming a 2^- valency for oxygen, it was originally thought that Cu(III) be present in both classes of high-T_c superconductors, $La_{2-x}M_xCuO_4$ (M = Sr, Ba; 2:1:4 compounds) and $MBa_2Cu_3O_7$ (M = Y or rare earths; 1:2:3 compounds). Subsequent photoemission results,[5-10] however, showed that the proportion of Cu(III) $3d^8$ is negligible in these compounds. In order to satisfy charge neutrality, it was therefore proposed that the excess holes required from oxygen stoichiometry are located in the oxygen ligand p band giving rise to O^- species.[5-7,9,10]

In the present paper we report on results of soft x-ray absorption (XA) studies at the Cu $L_{\text{II,III}}$ thresholds in a variety of high-T_c superconductors and related compounds. One advantage of XA spectroscopy, in comparison to photoemission, is that the method is more bulk sensitive. Comparing the XA near-edge fine-structure spectra of these compounds with those of CuO and $NaCuO_2$, we are able to establish that the holes in the Cu–O bonds reside primarily on the oxygen ligand sites, and that the amount of Cu(III)-$3d^8$ configuration in the ground state is negligible in these superconductors. These findings are essentially in conformity with previous conclusions from photoemission,[5-10] soft XA,[9,11] and electron-energy-loss spectroscopic studies.[12,13]

The investigated high-T_c compounds were prepared by the usual ceramic process starting with the component oxides along with $BaCO_3$, followed by oxygen annealing. All the samples were characterized by powder x-ray diffraction and were found to be single phase. We have also checked their superconducting properties by carrying out standard four-probe resistance measurements. The T_c values, for which the resistance dropped below the level of detection, are given in Table I. For comparison, we have also studied CuO and $NaCuO_2$. The preparation of $NaCuO_2$ has been described previously.[8] XA studies at the Cu $L_{\text{II,III}}$ thresholds were carried out in total-electron-yield mode at the double-crystal monochromator beamline of BESSY (Berlin) using a pair of beryl ($10\bar{1}0$) crystals, with a resolution of $\simeq$0.40 eV (full width at half maximum) at 940 eV. Special care was taken to avoid exposure of $NaCuO_2$ to air, which is known to be very unstable in the presence of moisture. The spectra were recorded after *in situ* scraping of the sample surfaces with a diamond file; no bake-out of the ultrahigh-vacuum chamber was performed in order to minimize oxygen loss.

In Fig. 1, we compare the $L_{\text{II,III}}$ XA spectra of $YBa_2Cu_3O_{7-\delta}$ with those of CuO and $NaCuO_2$. Two main groups of peaks, separated by the spin-orbit splitting of the $\underline{2p}_{3/2}$ (L_{III}) and $\underline{2p}_{1/2}$ (L_{II}) hole states, can be distinguished. The absolute energies were fixed by assuming a Cu L_{III} peak energy of 931.2 eV according to Koster.[14] Since the ground state of CuO is made up of $3d^9$ and $3d^{10}\underline{L}$ states ($\underline{L}$ = oxygen ligand hole), where the latter state arises from Cu $3d$-O $2p$ covalency,[15] the observed single final states at the $L_{\text{II,III}}$ XA thresholds are assigned to $\underline{2p}3d^{10}$ final-state configurations, with a Cu $2p$ electron being promoted to the Cu $3d$ orbital. Thus, the main peaks observed for $YBa_2Cu_3O_{7-\delta}$ at about the same energies of $\simeq$931 eV and $\simeq$951 eV are also assigned to

TABLE I. Ratio of intensity of peak B to that of peak A in the Cu-L_{III} XA spectra of the ternary copper-oxide superconductors studied, along with resistively determined transition temperatures T_c. ΔE denotes the separation between peaks B and A in eV. The following error bars are estimated: ±0.05 for I_B/I_A; ±0.5 K for T_c; ±0.08 eV for ΔE.

Compound	I_B/I_A	T_c (K)	ΔE (eV)
$YBa_2Cu_3O_7$	0.92	88	1.40
$Y_{0.9}Tb_{0.1}Ba_2Cu_3O_7$	0.94	82.5	1.40
$Y_{0.98}Ce_{0.02}Ba_2Cu_3O_7$	0.78	88	1.32
$La_{1.85}Sr_{0.15}CuO_4$	0.62	29	0.91
$La_{1.8}Ba_{0.2}CuO_4$	0.57	21	1.12

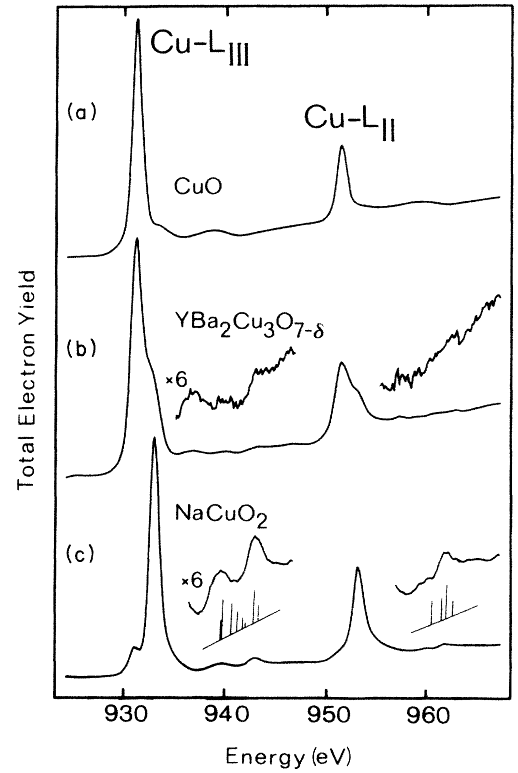

FIG. 1. Comparison of the soft XA spectrum of $YBa_2Cu_3O_{7-\delta}$ in the region of the Cu $L_{II,III}$ thresholds with those of CuO and $NaCuO_2$. The vertical scale is enhanced for $NaCuO_2$ and $YBa_2Cu_3O_{7-\delta}$ in the energy ranges of the $\underline{2p}3d^9$ final-state signals. The vertical-bar diagrams represent the expected multiplet structures of these final states at the L_{II} and L_{III} thresholds (from Ref. 15).

$\underline{2p}3d^{10}$ final states arising from a $3d^9$ initial-state configuration.

In formally trivalent $NaCuO_2$, the ground state—due to covalency—will be a mixture of $3d^8$, $3d^9\underline{L}$, and $3d^{10}\underline{L}^2$ configurations. The XA process may then give rise to two final states with $\underline{2p}3d^9$ and $\underline{2p}3d^{10}\underline{L}$ configurations, as observed [Fig. 1(c)]. The small shoulders seen at the leading edges of the main peaks are interpreted as signatures from Cu(II) impurities in the studied $NaCuO_2$ sample. Due to the $2p$ core hole-$3d$ Coulomb energy (U_{dc}), the $\underline{2p}3d^9$ final state is expected to be approximately U_{dc} above $\underline{2p}3d^{10}\underline{L}$, with $U_{dc} \simeq 9$ eV.[15] Thus, the main peaks in the $L_{II,III}$ spectrum of $NaCuO_2$ at $\simeq 933$ eV and $\simeq 953$ eV are assigned to $\underline{2p}3d^{10}\underline{L}$ final-state configurations, while the absorption peaks at $\simeq 941$ eV and $\simeq 944$ eV (L_{III}) and at $\simeq 963$ eV (L_{II}) come from $\underline{2p}3d^9$ final states. The spectrum in Fig. 1(c) represents the first observation of $\underline{2p}3d^9$ final states in the $L_{II,III}$ XA spectrum of any copper compound. Previous soft XA work failed in observing these $\underline{2p}3d^9$ final-state signals for other formally trivalent Cu compounds.[11,16] The relatively weak absorption lines in the spectrum of Fig. 1(c) exhibit the typical $2p^5 3d^9$ multiplet structures, which are indicated by the two vertical bar diagrams.[15]

This then strongly suggests that the shoulders observed on the trailing edges of the main peaks in the $L_{II,III}$ spectrum of $YBa_2Cu_3O_{7-\delta}$ [Fig. 1(b)] represent $\underline{2p}3d^{10}\underline{L}$ final states arising from a $3d^9\underline{L}$ initial-state configuration. It should be noted that Bianconi et al. observed similar shoulders in their $L_{II,III}$ XA spectra $YBa_2Cu_3O_{7-\delta}$, and reached essentially the same final-state assignment on the basis of a comparison with Cu $2p_{3/2}$ x-ray photoemission spectra of CuO.[11] In other previous soft XA work at the Cu $L_{II,III}$ thresholds of high-T_c materials, similar details could not be observed due to lower resolution.[9,17]

We now address the question of how much the Cu(III) $3d^8$ configuration is contained in the electronic ground state of $YBa_2Cu_3O_{7-\delta}$. Such an evaluation on the basis of the present spectra is possible since direct signals of the Cu(III)-$3d^8$ ground-state configuration have been identified for $NaCuO_2$ [Fig. 1(c)]. Though we cannot quantify the exact weight of the $3d^8$ configuration in the ground state of $NaCuO_2$ without considering configuration interactions,[18] we point out that a $\underline{2p}3d^9$ final state in XA can only rise from a $3d^8$ initial state. This then means that the electronic ground state of $NaCuO_2$ is predominantly made up of the $3d^9\underline{L}$ configuration with a smaller contribution from $3d^8$. A close inspection of the $L_{II,III}$ XA spectrum of $YBa_2Cu_3O_{7-\delta}$ [Fig. 1(b)] in the relevant energy range clearly shows that the proportion of any Cu(III) $3d^8$ configuration in the ground state of this high-T_c compound must be very small. Similar conclusions were recently drawn from electron-energy-loss spectroscopy studies[12,13] and from related photoemission[5-10] and soft XA work.[11]

In Fig. 2 we show the Cu L_{III} XA spectra of various 2:1:4 and 1:2:3 ternary copper oxide superconductors in detail. All the spectra exhibit a prominent white line at $\simeq 931$ eV (peak A), coinciding in energy with the single L_{III} line of CuO (see Fig. 1); in addition, all superconducting samples show a second broader shoulder at $\simeq 933$ eV (peak B). Peak B matches in energy quite well with the main L_{III} peak in $NaCuO_2$ that we assigned to a $\underline{2p}3d^{10}\underline{L}$ final state. The intensity of peak B is found to vary from one compound to the other: it is rather prominent for $YBa_2Cu_3O_{7-\delta}$, but only barely discernible for $La_{1.85}Sr_{0.15}CuO_4$ and $La_{1.8}Ba_{0.2}CuO_4$. T_c has been found to scale with oxygen deficiency in $YBa_2Cu_3O_{7-\delta}$.[19] This leads one to believe that it should also scale with the total number of ligand-band holes, a quantity which is accessible to the present technique by the intensity of peak B.

We have derived the relative intensities of peak B in the studied compounds by fitting the L_{III} spectra to a combination of two Lorentzians and a low-intensity background function. A typical decomposition in the component peaks and the underlying background is shown in Fig. 2. The resulting relative intensities and energy separations of peak B are presented in Table I along with the corresponding T_c's for all samples studied. The data clearly show that the intensity of peak B is substantially larger in the 1:2:3 compounds than in the 2:1:4 compounds. We also see from an inspection of Table I that T_c in the 1:2:3 series of compounds does not scale, within the present experimental accuracy, with the oxygen-hole concentration, as measured by the intensity of peak B.

A further interesting aspect of our observations con-

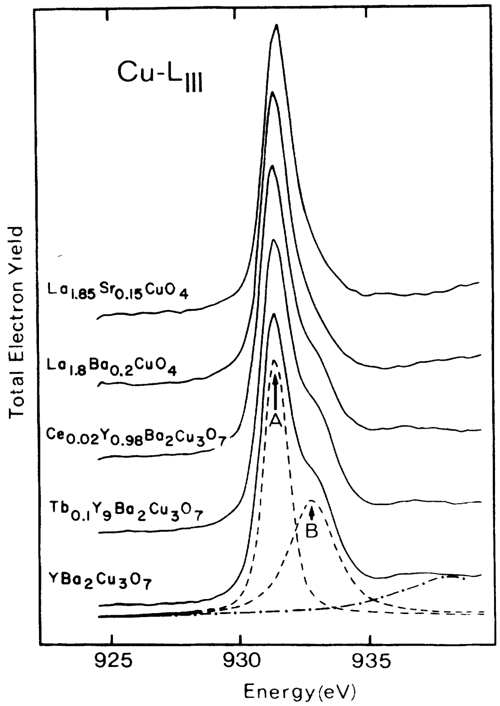

FIG. 2. XA spectra at the Cu L_{III} threshold for various high-T_c superconducting oxides. The decomposition of the $YBa_2Cu_3O_{7-\delta}$ spectrum in terms of two Lorentzians and an inelastic background, resulting from least-squares fit, is given by the dashed and dashed-dotted lines.

cerns the relative intensity of peak *B*, which exceeds the ligand-hole concentration derived from oxygen stoichiometry. If, e.g., seven oxygen atoms are assumed per formula unit for $YBa_2Cu_3O_{7-\delta}$ (with $\delta = 0$), a ratio of 1:2 between the formally trivalent and divalent copper species is expected. Spectroscopically, however, an intensity ratio close to 0.9 is observed for the 1:2:3 compounds as given by the relative intensity of peak *B*; this is almost 100% larger than the stoichiometry-derived ratio. Table I shows that similar observations are made for all superconducting compounds studied.

Having discussed the room-temperature XA spectra of these compounds, we point out that lowering the temperature to 80 K did not show any perceptible change in the spectral features. This is in contrast to reports on low-temperature photoemission studies of high-T_c superconductors, where considerable modifications in the spectral features were observed for $YBa_2Cu_3O_{7-\delta}$ and $La_{1.85}Sr_{0.15}CuO_4$.[6] The reported low-temperature changes in the photoemission spectra could be caused by surface effects due to the surface sensitivity of the technique, while the bulk intrinsic properties of these compounds, probed by XA, are not undergoing observable temperature-dependent modifications.

The main conclusion of the present soft XA studies concerning the electronic ground state of high-T_c superconductors is in full agreement with the results of other work.[5-13] The excess electronic holes required from oxygen stoichiometry are found to be mainly located in the oxygen-ligand band and not on the copper ions: this is concluded from the absence of soft XA signals from Cu(III) $3d^8$ initial states, while the dominating XA peak is made up of lines from Cu(III) $3d^9$ and Cu(III) $3d^9\underline{L}$ ground states. The present findings are particularly supported by recent results from high-resolution electron-energy-loss spectroscopy at the O 1*s* threshold, where dipole-allowed transitions into empty O 2*p* band states were observed.[13] They are also in accord with the results of recent core-level photoemission (PE) studies of 1:2:3 compounds by Steiner *et al.*[20] revealing relatively weak Cu 2*p* PE signals assigned to $\underline{2p}3d^{10}\underline{L}^2$ final states. This latter study also did not give any experimental evidence for signals from Cu(III) $3d^8$ initial states in the PE spectra, even though a Cu(III) $3d^8$ content was derived in an indirect way. The controversy concerning the possible trivalency of Cu in high-T_c superconductors is therefore mainly related to the question of whether Cu $3d^9\underline{L}$ components in the initial-state wave function should be termed trivalent or not. In any case, the present study gives no evidence for the presence of Cu(III) $3d^8$ configurations in the ground state of the studied high-T_c superconductors.

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