Unoccupied elecronic structure of Sr2CuO2Cl2 and Ba2Cu3O4Cl2: experiment and theory

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Unoccupied electronic structure of Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$: Experiment and theory

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The unoccupied electronic structure of the layered cuprates Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ has been studied using polarization-dependent x-ray absorption spectroscopy at the O 1$s$ and Cu 2$p_{3/2}$ edges and band-structure calculations within the local-density approximation. In contrast to almost all high-temperature superconductors, there are no oxygen atoms outside the Cu-O planes in these oxychlorides. Our results represent therefore direct experimental information regarding the oxygen-derived unoccupied electronic structure of undoped Cu-O planes in square-planar coordination. The O 1$s$ and Cu 2$p_{3/2}$ x-ray absorption spectra of Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ are quite similar with an essentially two-dimensional upper Hubbard band and extra oxygen and copper related absorption fine structure at higher energies. From its polarization dependence and a comparison to the results of the band-structure calculations, it is concluded that this extra fine structure is related to transitions into O 2$p$ and Cu 3$d_{3z^2-r^2}$ orbitals which have become partly unoccupied due to hybridization with Sr 4$d$/Ba 5$d$/Cu 4$p_z$ and Cu 4$s$ orbitals, respectively. Differences between these two compounds are the larger width of the upper Hubbard band and the higher relative Cu 3$d_{3z^2-r^2}$ hole occupation above the upper Hubbard band in Ba$_2$Cu$_3$O$_4$Cl$_2$. These differences can be related to the extra Cu$_{0.5}$ atoms in the Cu$_3$O$_4$ planes of Ba$_2$Cu$_3$O$_4$Cl$_2$ with respect to the CuO$_2$ planes of Sr$_2$CuO$_2$Cl$_2$. [S0163-1829(98)03706-0]

I. INTRODUCTION

The magnetic and electronic properties of layered cuprates (e.g., La$_2$CuO$_4$) have received much attention in recent years, because they are nearly ideal quantum antiferromagnets when undoped (and some of them) become high-temperature superconductors when doped. Crucial for their understanding is the knowledge of the energetically low-lying electronic structure of the CuO$_2$ planes [Fig. 1(a)], which are a structural element common to almost all of these materials. Electron energy-loss (EELS) and x-ray absorption spectroscopy (XAS) of layered cuprates have shown that the first electron-addition states of such cuprates, which are related to the upper Hubbard band (UHB), are dominated by Cu 3$d_{3z^2-r^2}$ and O 2$p_{x,y}$ orbitals with only a small admixture of out-of-plane Cu 3$d_{3z^2-r^2}$ and O 2$p_z$ orbitals; thus these materials represent nearly ideal two-dimensional quantum systems. The higher-lying O 2$p$-derived unoccupied electronic structure of the CuO$_2$ planes of most of the high-temperature superconductors is not directly accessible by XAS or EELS, because the O 2$p$-derived spectral weight in this energy range may be at least partially due to oxygen atoms located outside the CuO$_2$ planes (e.g., in the block layers). This problem does not exist in the copper oxyhalides $A_2$CuO$_2$X$_2$ and $A_2$Cu$_3$O$_4$X$_2$ ($A$: Ba, Sr; $X$: halide): they are layered cuprate compounds composed of Cu-O planes with no oxygen atoms located outside the Cu-O planes.

A representative of the $A_2$CuO$_2$X$_2$ compounds is the copper oxychloride Sr$_2$CuO$_2$Cl$_2$ which is a tetragonal antiferromagnetic insulator (Néel temperature 250 K), isostructural to the high-temperature phase of La$_2$CuO$_4$, but which has apical chlorine ions instead of apical oxygen ions. The Cu-Cl$_{apex}$ distance in Sr$_2$CuO$_2$Cl$_2$ (2.86 Å) (Ref. 2) is significantly larger than the Cu-O$_{apex}$ distance in La$_2$CuO$_4$ (2.42 Å) (Ref. 4) making it an interesting candidate for a model system describing the physics of an undoped CuO$_2$ plane because of the reduced influence of the out-of-plane ions on the CuO$_2$ planes. Magnetization and neutron scattering experiments$^{3,5}$ have indeed shown that Sr$_2$CuO$_2$Cl$_2$ can be regarded as the best experimental realization of the $S$ = 1/2 two-dimensional square lattice Heisenberg antiferromagnet known up to now. Although until now it was not possible to dope Sr$_2$CuO$_2$Cl$_2$ chemically in order to achieve a metallic or even superconducting state$^{6}$ (thus, strictly it is not a parent compound of a high-temperature superconductor), it is also an interesting model system for the study of aspects of high-temperature superconductivity, because in a photoemission experiment Sr$_2$CuO$_2$Cl$_2$ is hole doped by the photoionization process itself, such that the electronic structure of a CuO$_2$ plane in the low-doping limit can be studied. The energy-momentum relation of the hole thus created can be measured, which in the case of the lowest electron
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removal states corresponds to a determination of the dispersion of a Zhang-Rice singlet in an antiferromagnetic background (if the size of the “magnetic polaron” is much smaller than the antiferromagnetic correlation length)\(^9\). Experiments of this kind have not been possible up to now with the insulting parent compounds of the high-temperature superconductors, because they do not satisfy the high demands of photoemission spectroscopy on surface quality (in contrast to \(\text{Sr}_2\text{CuO}_2\text{Cl}_2\)).

Representatives of the \(A_2\text{Cu}_3\text{O}_4\text{X}_2\) compounds are the tetragonal insulators \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) and \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\).\(^10\) They are composed of \(\text{Cu}_3\text{O}_4\) planes [Fig. 1(b)] as fundamental building blocks, which in contrast to \(\text{Cu}_2\text{O}_2\) planes have two different copper sites: two-thirds of the Cu atoms \((\text{Cu}_A)\) occupy the Cu sites of the familiar \(\text{Cu}_2\text{O}_2\) plane, while one-third of the Cu atoms \((\text{Cu}_B)\) reside in the center of every second \(\text{Cu}_2\text{O}_2\) square. The distances from the \(\text{Cu}_A\) and \(\text{Cu}_B\) atoms to their apical ions \((\text{Cu}_A\text{-Cl}_{\text{apex}}: 3.46\,\text{Å}, \text{Cu}_B\text{-Ba}_{\text{apex}}: 4.99\,\text{Å})\) are even larger than the \(\text{Cu}_A\text{-Cl}_{\text{apex}}\) distance in \(\text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2\). These compounds exhibit interesting magnetic properties which are directly related to the existence of two different Cu sublattices. Two antiferromagnetic transition temperatures have been measured: the first transition occurring at 320 and 380 K for \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) and \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\),\(^11–13\) respectively. These temperatures are comparable to the Neél temperatures of other cuprates and are ascribed to antiferromagnetic order in the \(\text{Cu}_A\) sublattice. The second transition is at 30 K for \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) and 40 K for \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\),\(^11–13\) and marks the onset of antiferromagnetic order in the \(\text{Cu}_B\) subsystem. In the temperature range between the two antiferromagnetic transitions a weak in-plane ferromagnetic component has also been found which has been explained by a pseudodipolar coupling between the Cu subsystems in the case of \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\).\(^13\) According to magnetization and neutron scattering experiments,\(^13\) both the \(\text{Cu}_A\) and \(\text{Cu}_B\) subsystems of \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) represent further examples of \(S=1/2\) two-dimensional quantum antiferromagnets. The \(\text{Cu}_B\) subsystems of \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) and \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) are especially interesting because of their weak exchange interaction \((J\sim 10\) and 17 meV, respectively)\(^13,14\) which is an order of magnitude smaller than the exchange interaction normally encountered in systems of corner-sharing \(\text{CuO}_4\) plaquettes \((J\sim 125\) meV).\(^15\) These compounds also offer the exciting possibility of the determination of the dispersion of a Zhang-Rice singlet moving in an antiferromagnetic \((\text{Cu}_A\text{-O subsystem})\) and a paramagnetic \((\text{Cu}_B\text{-O subsystem})\) background in a single room-temperature photoemission experiment. This has been carried out for \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) (Ref. 8) and corresponds to the simultaneous study of the low- and high-doping limit of a \(\text{CuO}_2\) plane as far as the magnetic background is concerned. In this paper, we examine the unoccupied O 2p and Cu 3d-derived electronic structure of \(\text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2\) and \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) using polarization-dependent O 1s and Cu 2p\(_{3/2}\) XAS at room temperature and band-structure calculations in the local-density approximation (LDA).

II. EXPERIMENTAL AND THEORETICAL METHODS

\(\text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2\) single crystals were grown by the traveling-solvent floating-zone technique and had dimensions up to 10×5×1.5 mm. The \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\) single crystals were grown from the melt, their typical dimensions being 2.5×2×0.7 mm.

The XAS measurements were performed with linearly polarized synchrotron radiation obtained from the SX 700/II monochromator\(^16\) operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). Total electron yield (TEY) as well as fluorescence yield (FY) have been applied to monitor the absorption at the O 1s and Cu 2p edges, the energy resolution being set to 280 and 660 meV for the O 1s and Cu 2p absorption thresholds, respectively. Cleaved and as-grown surfaces were used for the FY measurements of \(\text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2\) and \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\), respectively. For the surface-sensitive TEY measurements only cleaved surfaces were used. The single crystals were cleaved \textit{in situ} at a base pressure of 2×10\(^{-10}\) mbar by means of a cantilever attached to the top of the sample, resulting in a cleavage plane which is parallel to the \(\text{CuO}_2/\text{Cu}_3\text{O}_4\) planes. All measurements were performed at room temperature.

In order to study the polarization dependence of the XAS signal, different angles of incidence of the x-ray beam with respect to the \(\text{CuO}_2/\text{Cu}_3\text{O}_4\) planes were used. In the geometry of normal incidence, the electric-field vector of the incoming radiation lies in the \(\text{CuO}_2/\text{Cu}_3\text{O}_4\) planes ("in-plane geometry"). In the case of \(\text{Sr}_2\text{Cu}_2\text{O}_2\text{Cl}_2\), spectra for the electric-field vector perpendicular to the \(\text{CuO}_2\) planes ("out-of-plane geometry") were extrapolated from measurements at grazing incidence at three different incidence angles \((50°, 55°, 65°)\) with respect to the \(\text{CuO}_2\) planes. In the case of \(\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2\), FY measurements in out-of-plane geometry were performed at a side face of the crystals at normal incidence. The data have been corrected for the time dependence of the incident photon flux by means of the simultaneously measured ring current of the synchrotron. The energy dependence of the incident photon flux was taken into account via division by an XAS spectrum of a clean gold foil recorded in the same energy range. A linear background has been subtracted. Additionally, the spectra were normalized to calculated atomic O 1s and Cu 2p\(_{3/2}\) photoionization cross...
sections$^{17} - 70$ eV above the absorption threshold. This far above the threshold, the final states are practically free-electron-like and thus isotropic. Self-absorption effects were taken into account according to a procedure described elsewhere,$^{18}$ and the energy calibration was checked by comparison of CuO Cu 2$p_3/2$ TEY data measured during these experiments with corresponding data in the literature.$^{19}$

The density of states (DOS) and the partial DOS for both compounds were calculated in the LDA using the linear combination of atomic orbitals method. Due to the relatively open structures, four and eight empty spheres per unit cell have been introduced for Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$, respectively. The calculations are scalar relativistic and a minimal basis was chosen consisting of Cu(4$s$,4$p$,3$d$), O(2$s$,2$p$), Ba(6$s$,6$p$,5$d$), Sr(5$s$,5$p$,4$d$), and Cl(3$s$,3$p$). The lower-lying states were treated as core states. To optimize the local basis a contraction potential has been used at each site.$^{20}$ The Coulomb part of the potential was constructed as a sum of overlapping spherical contributions and the exchange and correlation part was treated in the atomic-sphere approximation. The orbital-projected partial DOS and the corresponding hole occupation numbers are calculated as net quantities. In order to facilitate comparison with experiment, the calculated partial DOS were broadened by convolution with a Lorentzian and a Gaussian to account for lifetime effects and the experimental energy resolution, respectively. A linear energy dependence of the lifetime was assumed.

III. RESULTS AND DISCUSSION

In XAS experiments, core electrons are excited into unoccupied states by absorption of photons. This leaves the solid in an excited state which decays via emission of fluorescence photons (FY) or electrons (TEY), whose intensity is measured as a function of the energy of the incoming photons. The mean escape depth of the electrons is of the order of 10 Å. Therefore TEY is a surface-sensitive method in contrast to FY which probes bulk properties (mean escape depth of soft-x-ray photons: 10 000 Å). As core electrons are localized, the local unoccupied electronic structure is probed (XAS is site-selective). The transitions of the core electrons into the unoccupied states are governed by dipole selection rules. Therefore, in recording an O 1$s$ (Cu 2$p$) x-ray absorption spectrum one measures mainly the O 2$p$ (Cu 3$d$) orbital contributions to the matrix-element weighted unoccupied density of states,$^{21}$ under the supposition that the influence of the core hole in the final state on the x-ray absorption spectrum can be neglected. It is generally accepted that O 1$s$ x-ray absorption spectra of cuprates are not distorted by the interaction with the core hole. This is not true for Cu 2$p$ x-ray absorption spectra, where spectral weight is shifted from higher energies to the threshold due to the interaction of the localized excited $d$-electron with the core hole to give the so-called ‘white-line.’$^4$ The spectral weight thus no longer reflects the detailed shape of the unoccupied Cu 3$d$ derived electronic structure, but its intensity is nevertheless related to the number of holes in the Cu 3$d$ shell.$^4$ The usage of polarized radiation and a single-crystalline sample imposes further restrictions on the symmetry of the unoccupied states which are observable in an absorption spectrum: if the electric-field vector is in the CuO$_2$/Cu$_3$O$_4$ plane, there are only contributions from unoccupied in-plane $p$ orbitals ($p_x$, $p_y$) and unoccupied in- and out-of-plane $d$ orbitals ($d_{3z^2-r^2}$, $d_{xy}$, $d_{xz}$, $d_{yz}$) to the O 1$s$ and Cu 2$p$ x-ray absorption spectra, respectively, while for the electric-field perpendicular to the CuO$_2$/Cu$_3$O$_4$ planes only out-of-plane orbitals ($p_{z}$, $d_{3z^2-r^2}$) are probed.$^4$

Figures 2 and 3 present polarization-dependent O 1$s$ x-ray absorption spectra (FY) of Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ for in- and out-of-plane geometry. In addition, calculated Sr 4$d$/Ba 5$d$, O 2$p_{x,y}$, O 2$p_z$, and Cu 4$p_z$ partial DOS are shown. All of the calculated partial DOS are shifted in energy by the amount necessary to get best agreement between the calculated O 2$p$ partial DOS and experiment. The overall shape of the experimental O 1$s$ x-ray absorption spectra is essentially the same for both compounds: they consist of a broad absorption feature at $\sim 534$ and $\sim 533$ eV and a prepeak at 529.4 and 529.8 eV for Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$, respectively. Both compounds show anisotropy in intensity between absorption spectra taken in in- and out-of-plane geometry; this is especially distinct in the case of the prepeaks, which are considerably stronger when the electric-field vector is in-plane.

The prepeaks are associated with the O 2$p_z$ contributions to the upper Hubbard band,$^3$ and the anisotropy between in-plane and out-of-plane geometry reveals that these are predominantly from in-plane oxygen orbitals (O 2$p_x$, O 2$p_y$),
while out-of-plane oxygen orbitals (O 2p) contribute significantly less. A comparison of the spectral weights of the prepeaks for in- and out-of-plane geometry yields values of 0.13 (Sr$_2$CuO$_2$Cl$_2$) and 0.09 (Ba$_2$Cu$_3$O$_4$Cl$_2$) for the ratio of the O 2p to the total O 2p contributions to the upper Hubbard band, these values are comparable to that measured in the cuprate high-temperature superconductors.$^1$ One has to keep in mind that the values given for the relative contributions of the out-of-plane orbitals are upper limits because of the possibility of a small misorientation of the crystals and the finite degree of linear polarization of the radiation (97%), so the true values may even be smaller. In Table I the calculated hole occupation numbers of the O 2p, Cu 3d, Cu 4s, and Cu 4p orbitals are given. No O 2p orbital contribution to the UHB is found for both compounds which is in qualitative agreement with the experimental results. Two remarks concerning the result of the calculations have to be made:

(a) The calculations predict a paramagnetic and metallic behavior. This is a typical result for an LDA calculation and shows the necessity to deal with the electron correlations in a more direct way. However for the higher-lying unoccupied DOS considered here the correlations are not so important due to the small Cu 3d character of the higher lying bands. The main feature which will occur if we introduce the correlations explicitly is the splitting of the bands crossing the Fermi level into a lower and an upper Hubbard band (UHB). The hole occupation number for a certain orbital contribution to the UHB is therefore calculated by summing up the corresponding partial DOS from the Fermi level to the upper band edge of the Cu 3d$_{2−y^2}$−O 2p$_{x,y}$ band.

(b) The calculated O 2p hole occupation numbers are given for symmetrized oxygen orbitals (linear combinations of two oxygen orbitals). This means that in the case of the UHB of Sr$_2$CuO$_2$Cl$_2$ the value given for the hole occupation number of the O 2p$_{x,y}$ orbitals has to be multiplied by a factor of 2, because only one oxygen orbital per symmetrized orbital is hybridized with a Cu 3d$_{2−y^2}$ orbital.$^{22}$

Returning to the XAS spectra, the prepeak of the Ba$_2$Cu$_3$O$_4$Cl$_2$ O 1s x-ray absorption spectrum is considerably broader (full width at half maximum, FWHM = 1.6 eV) than its Sr$_2$CuO$_2$Cl$_2$ counterpart (FWHM = 1.1 eV) and has gained ∼20% in spectral weight. Its shape is consistent with the presence of two peaks associated with the UHB’s of the Cu$_A$-O and Cu$_B$-O networks which are energetically slightly offset. As all oxygen sites in Ba$_2$Cu$_3$O$_4$Cl$_2$ are equivalent, this shift must be related to a difference in the energies of the Cu$_A$ and the Cu$_B$ 3d$_{2−y^2}$ levels, a finding which has also been deduced from a tight-binding fit to an LDA bandstructure calculation from which an energy difference of ∼0.4 eV was found.$^{14}$

In the O 2p-derived absorption fine structure above the UHB (above 532 eV), there are marked differences between Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$: in Sr$_2$CuO$_2$Cl$_2$ a rather isotropic peak is visible at ∼534 eV, while its counterpart in Ba$_2$Cu$_3$O$_4$Cl$_2$ is located at ∼533 eV and is much stronger in out-of-plane than in in-plane geometry. Above 533/534 eV the O 1s x-ray absorption spectra of Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ are qualitatively similar with both having more spectral weight due to O 2p$_{x,y}$ than O 2p$_z$ orbitals.

The occurrence of O 2p-derived absorption fine structure above the UHB is not compatible with models of the low-lying unoccupied electronic structure of the Cu-O planes of layered cuprates which only take into account hybridization between the O 2p$_{x,y}$ and the Cu 3d$_{2−y^2}$ orbitals. Therefore there must be additional hybridization of O 2p orbitals with

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**TABLE I.** Calculated total number of holes in the Cu 3d, Cu 4p, Cu 4s, and O 2p orbitals for Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$, and the corresponding hole numbers for the upper Hubbard band alone.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Sr$_2$CuO$_2$Cl$_2$</th>
<th>Ba$_2$Cu$_3$O$_4$Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHB</td>
<td>Total</td>
<td>UHB</td>
</tr>
<tr>
<td>Cu$<em>A$ 3d$</em>{2−y^2}$</td>
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<td>0.48</td>
</tr>
<tr>
<td>Cu$<em>B$ 3d$</em>{2−y^2}$</td>
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<td>0.34</td>
</tr>
<tr>
<td>Cu$<em>A$ 3d$</em>{xy}$</td>
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<td>0.02</td>
</tr>
<tr>
<td>Cu$<em>B$ 3d$</em>{xy}$</td>
<td>0.74</td>
<td>0.75</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Cu$<em>B$ 3d$</em>{xy}$</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Cu$<em>A$ 4p$</em>{x,y}$</td>
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<td>1.92</td>
</tr>
<tr>
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<td>1.94</td>
</tr>
<tr>
<td>Cu$_A$ 4p$_z$</td>
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</tr>
<tr>
<td>Cu$_B$ 4p$_z$</td>
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</tr>
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</tr>
<tr>
<td>O 2p$_z$</td>
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<td>0.20</td>
</tr>
</tbody>
</table>

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FIG. 3. O 1s x-ray absorption spectra of Ba$_2$Cu$_3$O$_4$Cl$_2$. •: electric-field vector in the Cu$_A$O$_4$ plane; -O: electric-field vector perpendicular to the Cu$_A$O$_4$ plane. The solid lines show calculated O 2p and O 2p$_z$ partial DOS as indicated in the figure. In order to illustrate hybridization effects the calculated Ba 5d and Cu$_A,B$ 4p$_z$ partial DOS are included as dotted lines. They should not be directly compared with the experimental data which are a measure of the unoccupied O 2p partial DOS. The DOS curves are broadened for lifetime effects and resolution and are shifted in energy to facilitate comparison with experiment (for details see text).
orbital contributions to the absorption fine structure above the UHB is close to unity. For the calculated O\(^{2-}\), Cu\(^{2+}\), and Sr\(^{2+}\) partial DOS, all of the orbitals other than the Cu \(3d_{x^2−y^2}\) have their origin in the presence of the extra Cu\(_A\) atoms and the correspondingly more closed structure of the Cu\(_A\) planes in Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\); because of the extra hybridization of O\(2p_x, y\) orbitals with the Cu\(_B\) 3d\(_{x^2−y^2}\) orbitals, the hybridization with the Ba \(5d\) orbitals is weaker than it would be without the Cu\(_B\) atoms. Therefore the spectral weight in the O \(1s\) x-ray absorption spectrum, which is related to the hybridization of the alkaline-earth atoms with the O \(2p_{x, y}\) orbitals, is smaller (or even absent as the peak at 534 eV) in Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) compared to Sr\(_2\)Cu\(_2\)O\(_2\)Cl\(_2\), while the UHB-related spectral weight is larger. The larger alkaline-earth-oxygen distance in Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) \((d_{Ba-O}: 2.74 \text{ Å}, d_{Sr-O}: 2.6 \text{ Å})\) may reinforce this effect.

Figures 4 and 5 present the polarization-dependent Cu \(2p_{3/2}\) x-ray absorption spectra of Sr\(_2\)Cu\(_2\)O\(_2\)Cl\(_2\) (TEY) and Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) (FY) for in- and out-of-plane geometry. The Cu \(2p_{3/2}\) partial DOS are shifted in energy by the amount necessary to get the best agreement between the calculated partial DOS and experiment. FY measurements are shown for Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\), because it was not possible to perform TEY measurements in out-of-plane geometry on the Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) single crystals: they were too small for grazing incidence measurements at the cleavage plane of the crystals. On the other hand, there was no possibility of the preparation of a cleavage plane at 90° to the Cu\(_3\)O\(_4\) planes where TEY measurements in an out-of-plane geometry could be accomplished by a normal-incidence measurement. For the FY mode cleaved surfaces are not necessary, we have therefore performed the Cu \(2p_{3/2}\) x-ray absorption spectra in in- and out-of-plane geometry in the FY mode on as-grown surfaces.
of the Ba$_2$Cu$_3$O$_4$Cl$_2$ crystals. The white line of the Cu 2p$_{3/2}$ x-ray absorption spectrum of Ba$_2$Cu$_3$O$_4$Cl$_2$ is especially affected by self-absorption effects because of its high intensity. A comparison of the Cu 2p$_{3/2}$ FY and TEY spectra taken in in-plane geometry shows that the FY in-plane spectra after correction for self-absorption are nevertheless equivalent to their TEY counterparts. For the Cu 2p$_{3/2}$ absorption spectra recorded in out-of-plane geometry in the FY mode, there are no pronounced self-absorption effects expected because of the low intensity. We assume therefore in the following that we can rely on the relative intensities of the Ba$_2$Cu$_3$O$_4$Cl$_2$ Cu 2p$_{3/2}$ FY spectra.

The experimental spectra show a narrow peak at 931.4 eV (the white line), which is associated with the Cu 3d contributions to the upper Hubbard band. The spectral weights of the white lines recorded in in-plane geometry are much larger than those in out-of-plane geometry, showing that the Cu 3d contributions to the upper Hubbard band are also mainly from in-plane Cu 3d$_{x^2}$ orbitals. A comparison of the spectral weights of the white lines recorded in in- and out-of-plane geometry yields for the ratio of the Cu 3d$_{x^2}$ orbital contribution to the total Cu 3d orbital contribution a value of 0.05 for both Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$.25 The white line of Ba$_2$Cu$_3$O$_4$Cl$_2$ is (as in the case of the prepeak of the O 1s x-ray absorption spectra) significantly broader (FWHM= 1.6 eV) than that of Sr$_2$CuO$_2$Cl$_2$ (FWHM=1.1 eV). This again is related to the presence of the extra Cu$_B$-O network in Ba$_2$Cu$_3$O$_4$Cl$_2$.

The Cu 2p$_{3/2}$ x-ray absorption spectra of Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ also show—besides the white line—a strongly polarization-dependent absorption step at 938 and 936 eV, respectively. According to the observed polarization dependence and matrix elements, these steps must be related to transitions mainly into unoccupied Cu 3d$_{x^2-y^2}$ states. The two steps differ in their shapes and their relative intensities:

(a) there is one peak and one shoulder visible in the Sr$_2$CuO$_2$Cl$_2$ absorption step (at 938.6 and 936.7 eV, respectively), while there are two peaks in the case of Ba$_2$Cu$_3$O$_4$Cl$_2$ at 936.5 and around 940.7 eV.

(b) the ratio of the integrated Cu 3d$_{x^2-y^2}$-derived spectral weight of these absorption steps to the integrated Cu 3d$_{x^2}$-derived spectral weight of the UHB (Ref. 25) is 0.24 and 0.47 for Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$, respectively.

Absorption steps of this kind have also been seen in other cuprates. From a comparison to the calculated partial DOS we conclude that (in the case of Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ at least) they are due to Cu 3d$_{x^2}$ states which become unoccupied by hybridization with Cu 4s states, because the calculated Cu 3d$_{x^2}$-derived DOS show excellent mutual agreement in shape and energetic position. Furthermore it is evident that the first peak in the absorption step of Ba$_2$Cu$_3$O$_4$Cl$_2$ at ~ 936.5 eV is dominated by contributions from Cu$_B$ 3d$_{x^2}$ orbitals hybridized with Cu$_4$ 4s orbitals, while the peak at 940.7 eV is from 3d$_{x^2}$ orbitals from either Cu$_A$ and Cu$_B$ which are hybridized with Cu$_4$ 4s and Cu$_B$ 4s orbitals, respectively. The ratios of the calculated total Cu 3d$_{x^2}$ to the calculated total Cu 3d$_{x^2}$ hole occupation numbers (0.10 and 0.44 for Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$, respectively) confirm the experimental results qualitatively and in the case of Ba$_2$Cu$_3$O$_4$Cl$_2$ even quantitatively. A possible cause for the difference in the Cu 3d$_{x^2}$ anisotropy between the two compounds could be again the more closed structure of a Cu$_3$O$_4$ plane with respect to a CuO$_2$ plane.

IV. SUMMARY

To summarize the results, direct experimental information about the unoccupied electronic structure of isolated undoped Cu-O planes in the environment of layered cuprates has been presented. The unoccupied electronic structures of Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ are very similar. The UHB’s are dominated by contributions from O 2p$_{x,y}$ and Cu 3d$_{z^2}$ orbitals thus being electronically two-dimensional as is the case for the UHB’s of the high-temperature superconductors. The most important finding of this work is that hybridization with Cu 3d$_{x^2}$ orbitals is not the only mechanism by which the O 2p orbitals of these oxychlorides become partly unoccupied. Comparison to calculated partial DOS data reveals that intra- and interplane hybridization with Cu 4p$_z$ and Sr 4d/Ba 5d orbitals is also important.

These results are directly relevant to the high-temperature superconductors because of the close similarity of the copper oxychlorides to their undoped parent compounds. Therefore the absorption fine structure encountered in the high-temperature superconductors in the O 1s x-ray absorption spectra above the UHB (Ref. 1) is not solely due to oxygen atoms located outside the CuO$_2$ planes (e.g., in the block layers) but is also derived from oxygen atoms in the Cu-O
planes. In the Cu $2p_{3/2}$ XAS spectra there are transitions into 
the Cu $3d_{x^2-r^2}$ orbitals at energies above the UHB, which have 
also been detected in the Cu $2p_{3/2}$ x-ray absorption spectra of 
the high-temperature superconductors. From a comparison to 
calculated partial DOS data we conclude that this is due to 
hybridization with Cu 4$s$ orbitals. Differences between 
Sr$_2$CuO$_2$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ are the larger width of 
the UHB and higher relative Cu $3d_{x^2-r^2}$ hole occupation above 
the UHB (with respect to the Cu $3d_{x^2-r^2}$ hole occupation in 
the latter compound). These differences can be 
thought of being a consequence of the extra Cu$_B$ atoms in the 
Cu$_3$O$_2$ planes of Ba$_2$Cu$_3$O$_4$Cl$_2$.

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1 J. Fink, N. Nücker, E. Pellegrin, H. Romberg, M. Alexander, and 
M. Knupfer, J. Electron Spectrosc. Relat. Phenom. 66, 395 
(1994).

2 L. L. Miller, X. L. Wang, S. X. Wang, C. Stassis, D. C. Johnston, 

3 D. Vaknin, S. K. Sinha, C. Stassis, L. L. Miller, and D. C. 

4 C. Almasan and M.B. Maple, in Chemistry of High-Temperature 
Superconductors, edited by C. N. R. Rao (World Scientific, Sin-

5 M. Greven, R. J. Birgeneau, Y. Endoh, M. A. Kastner, B. Keimer, 
72, 1096 (1994).

6 There is superconductivity in Sr$_2$CuO$_2$F$_{2+\delta}$ [$T_C = 46$ K, M. Al-
Mamouri, P. P. Edwards, C. Greaves, and M. Slaski, Nature 
(London) 369, 382 (1994)] and (Ca$_2$Na)$_2$CuO$_4$Cl$_2$ 
[$T_C = 26$ K, Z. Hiroi, N. Kobayashi, and M. Takano, ibid. 371, 
139 (1994)], which are closely related to Sr$_2$Cu$_2$O$_4$Cl$_2$.


8 M. S. Golden, H. C. Schmelz, M. Knupfer, S. Haffner, G. Krab-
bes, J. Fink, V. Y. Yushankhai, H. Rosner, R. Hayn, A. Müller, 

9 B. O. Wells, Z.-X. Shen, A. Matsura, D. M. King, M. A. Kast-
ner, M. Greven, and R. J. Birgeneau, Phys. Rev. Lett. 74, 964 

419, 58 (1976).

11 S. Noro, H. Suzuki, and T. Yamada, Solid State Commun. 76, 
711 (1990); S. Noro, T. Kouchi, H. Harada, T. Yamada, M. 


13 F. C. Chou, A. Aharony, R. J. Birgeneau, O. Entin-Wohlman, M. 
Greven, A. B. Harris, M. A. Kastner, Y. J. Kim, D. S. Kleinberg, 


16 M. Domke, T. Mandel, A. Puschmann, C. Xue, D. A. Shirley, G. 
Kaindl, H. Petersen, and P. Kuske, Rev. Sci. Instrum. 63, 80 


18 J. Jaklevic, J. A. Kirby, M. P. Klein, and A. S. Robertson, Solid 
State Commun. 23, 679 (1977); L. Tröger, D. Arvanitis, K. Bab-


20 H. Eschrig, Optimized LCAO Method (Springer-Verlag, Berlin, 
1989).

21 Transitions into unoccupied Cu 4$s$ orbitals are also allowed, but 
the probability is smaller by a factor of 20 [see, for example, B. 
The Cu $2p_{3/2}$ x-ray absorption spectra are therefore dominated 
by contributions due to transitions into unoccupied Cu 3$d$ orbit-
als, the unoccupied Cu 4$s$ orbitals being not visible in the spec-
tra but influencing them via their hybridization with the Cu 
3$d_{x^2-r^2}$ orbitals as discussed later in this section.

22 This is not the case for Ba$_2$Cu$_3$O$_4$Cl$_2$ because of the extra hybrid-
ization with the Cu$_B$ 3$d_{x^2-r^2}$ orbitals.

23 The hole occupation number above the UHB is the total hole 
occupation number minus the hole occupation number in the 
UHB given in Table I.

24 The integration was carried out in the same energy range as for 
the calculated partial DOS.

25 Matrix element effects have been taken into account.