Unoccupied electronic structure of Li$_2$CuO$_2$

R. Neudert, H. Rosner, S.-L. Drechsler, M. Kielwein, M. Sing, Z. Hu, M. Knupfer, M. S. Golden, and J. Fink
Institut für Festkörper- und Werkstofforschung Dresden, P.O. Box 270016, D-01171 Dresden, Germany

N. Nücker, M. Merz, and S. Schuppler
Forschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, P.O. Box 3640, D-76021 Karlsruhe, Germany

N. Motoyama, H. Eisaki, and S. Uchida
Department of Superconductivity, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

M. Domke and G. Kaindl
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

We have investigated the unoccupied electronic structure of quasi-one-dimensional Li$_2$CuO$_2$ using polarization-dependent x-ray absorption spectroscopy. Although an isotropic ''in-plane'' situation is expected for the O $1s$ absorption edge, due to the single oxygen site in the edge-sharing chain geometry, we observe a clear energy shift of peaks derived from the upper Hubbard band, dependent on the direction of the light polarization. For the possible explanation of this observed shift, alternative scenarios are discussed, based upon the electronic structure as obtained from calculations within the local-density approximation, the effects of coupling to phonons during the core-level excitation process, as well as on the polarization-dependent charge distribution in the final state resulting in varying contributions from intersite electron-electron interactions. [S0163-1829(99)14939-7]

Quasi-one-dimensional (1D) cuprates have become important model systems for the study of electronic correlations in low dimensions and represent a useful starting point at which to obtain basic information relevant to the more complex behavior displayed by the related high-T_c superconductors and ladder systems. Among the large family of chain and ladder networks,[1] the simple straight chains are essential as they appear as building blocks in all of these materials. They can be classified structurally into two types, namely chains formed by CuO$_4$ plaquettes connected via shared corners ''corner-sharing chain'' or shared edges ''edge-sharing chain.'' The former is realized in Sr$_2$CuO$_3$, the unoccupied electronic structure of which has been studied recently.[2] The edge-sharing chain occurs in other insulating cuprates such as Li$_2$CuO$_2$, the spin-Peierls compound GeCuO$_3$, and the ladder-type material La$_6$Ca$_8$Cu$_24$O$_{41}$. The latter represents the undoped parent compound of Sr$_{0.4}$Ca$_{13.6}$Cu$_{24}$O$_{41.84}$, which exhibits superconductivity under high pressure.[3] Within the class of materials with edge-sharing chains, at first glance Li$_2$CuO$_2$ seems to be an ideal model substance since in this case the CuO$_2$ chain is the only building block in the crystal structure apart from the Li counter ions, and thus a direct access to properties connected with the chain geometry alone is possible. In contrast to the corner-sharing case, where a 180° Cu-O-Cu exchange path implies an antiferromagnetic (AF) nearest-neighbor Cu spin interaction ($J_1 > 0$), the ideal edge-sharing geometry results in a 90° Cu-O-Cu interaction, which favors a ferromagnetic (FM) spin interaction ($J_1 < 0$) between the Cu sites.[4] At the same time, the exchange path Cu-O-O-Cu plays a more important role, leading to an AF next-nearest-neighbor interaction, J_2, and thus to frustration. For Li$_2$CuO$_2$, with an Cu-O-Cu angle

of $\theta = 94°$, exchange constants of $J_1 = -100$ K and $J_2 = 62$ K have been obtained from magnetic susceptibility data and an analysis within a standard pd model.[5] Besides the magnetic order along the chain direction (crystallographic **a** direction), Li$_2$CuO$_2$ shows a three-dimensional magnetic structure. Different chains in the (**a,c**) plane are FM ordered, whereas in the **b** direction one finds an AF coupling of the different layers of chains.[6] A detailed knowledge of the electronic structure of Li$_2$CuO$_2$ is necessary to understand the fundamentals of these magnetic properties.

In this contribution we study the unoccupied electronic structure of Li$_2$CuO$_2$ by means of polarization dependent x-ray absorption spectroscopy and discuss the results in the light of the predictions of LDA band-structure calculations.

Single crystals were grown using the traveling-solvent floating-zone method. Li$_2$CuO$_2$ adopts an orthorhombic crystal structure with lattice parameters $a = 2.86$ Å, $b = 9.39$ Å, $c = 3.66$ Å.[6] Note that we have interchanged the notation of the axes with respect to Ref. 6 for the convenience of the reader. Following our convention, the **c** direction is now perpendicular to the planar CuO$_4$ plaquettes as in the layered cuprates, and the chain direction lies along the **a** direction. Depending on the coordinate system adopted in the (**a,b**) plane, the orbitals relevant for the discussion below are denoted by O $2p_{x'}$, O $2p_{y'}$, Cu $3d_{x'^2-y'^2}$ in the case of (x',y') axes along the Cu-O bonds as sketched in Fig. 1(a), and O $2p_x$, O $2p_y$, Cu $3d_{xy}$ for axes parallel to the crystallographic directions [(x,y) axes, Fig. 1(b)]. The orientation of the crystals with a typical size of $3 \times 2 \times 1$ mm^3 was determined using x-ray diffraction. The x-ray absorption spectroscopy (XAS) experiments were carried out at the SX700/II
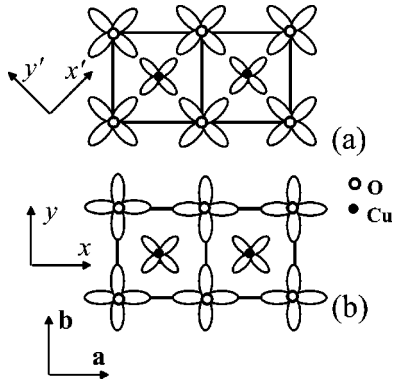
FIG. 1. A sketch of the edge-sharing chain in Li_2CuO_2. The directions **a** and **b** refer to the crystallographic axes. Cu and O orbitals are shown for two different coordinate systems: (a) axes of coordinates along the Cu-O bonds (x', y' axes) with O $2p_{x'}$, O $2p_{y'}$, and Cu $3d_{x'^2-y'^2}$ orbitals. (b) Axes of coordinates rotated by 45° (x,y axes) with O $2p_x$, O $2p_y$, Cu $3d_{xy}$ orbitals.

FIG. 2. Cu $2p_{3/2}$ absorption edges of Li_2CuO_2 for the electric-field vector **E** parallel to the three crystallographic axes.

beamline[7] operated by the Freie Universität Berlin at BESSY with an energy resolution of the monochromator of 280 and 660 meV at the O $1s$ and Cu $2p$ absorption thresholds, respectively.

Li_2CuO_2 is extremely hygroscopic. To ensure high surface quality we have performed our measurements on *in situ* cleaved samples at a base pressure of 5×10^{-10} mbar. For the O $1s$ and Cu $2p$ absorption spectra we chose the fluorescence yield (FY) and total electron yield (TEY) detection mode, respectively.[8] Energy calibration was performed by comparison of the Cu $2p_{3/2}$ XAS signal of a CuO sample with corresponding data in the literature.[9] In all cases the data were corrected for the energy-dependent incident photon flux and, in the case of O $1s$, for self-absorption effects following a procedure described elsewhere.[10] The spectra for different crystal orientations[11] are normalized ~ 80 eV above the absorption threshold, where the final states are nearly free-electron-like and therefore essentially isotropic.

XAS provides information on the character and symmetry of the unoccupied electronic states of solids and has played an important role in the investigation of cuprate-based materials.[12] Dipole selection rules and the localized initial core states enable a site specific study of the hole distribution. In addition, by using linearly polarized synchrotron radiation and single crystalline samples, orbitals with different symmetry can be probed by appropriately aligning the sample with respect to the electric field vector **E** of the incoming radiation. For example, in the geometry **E**∥**a** one selects only O $1s \rightarrow$ O $2p_x$ transitions [Fig. 1(b)].

To obtain some insight into the electronic structure from the theoretical point of view we have performed local-density approximation (LDA) calculations using the linear combination of atomiclike orbitals. Due to the relatively open structure, two empty spheres per unit cell have been introduced. The calculation was scalar relativistic and we have chosen a minimal basis set consisting of the Cu ($4s,4p,3d$), O ($2s,2p$), and Li ($2s,2p$) orbitals, the lower lying states being treated as core states. To optimize the local basis, a contraction potential has been used at each site.[13] The Coulomb part of the potential was constructed as a sum of overlapping extended site potentials, while the exchange
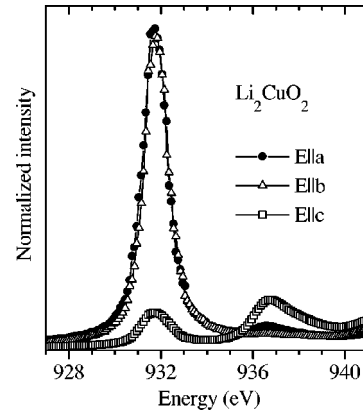
and correlation part was treated in the atomic-sphere approximation. The calculation of the orbital-projected net densities of states is described in detail elsewhere.[14] The calculation shows a paramagnetic and metallic behavior, with one isolated band crossing the Fermi level. Due to strong on-site electron correlations ignored in LDA, this antibonding band will split in an upper and a lower Hubbard band in accord with the experimentally observed insulating behavior.

Figure 2 shows the polarization-dependent Cu $2p_{3/2}$ x-ray absorption spectra of Li_2CuO_2. A narrow peak at ~ 931.8 eV (the so called ''white line'') is observed, which can be ascribed to the Cu $3d$ contributions to the upper Hubbard band (UHB).[12,15] As expected from the isotropic neighborhood of the Cu ion within the (**a**, **b**) plane (Fig. 1), almost identical spectra for **E**∥**a** and **E**∥**b** are observed. A completely different variation in intensity is found for light polarization perpendicular to the CuO_4 units (**E**∥**c**). The strong anisotropy of the white line between the in-plane [**E**∥(**a**,**b**)] and out-of plane (**E**∥**c**) geometry implies that the low-lying Cu $3d$ derived unoccupied states have predominantly Cu $3d_{xy}$ character, with only less than 7% of the intrinsic hole density located in out-of-plane orbitals (Cu $3d_{3z^2-r^2}$).[16]

Besides the white line, a strongly polarization-dependent absorption feature is found at 936.8 eV. Features in this energy range in the out-of-plane geometry have been seen in many other cuprates[12] and can be attributed to transitions into Cu $3d_{3z^2-r^2}$ orbitals which become partly unoccupied via hybridization with empty Cu $4s$ states.[17]

Turning to oxygen, we show in Fig. 3 the O $1s$ absorption edges for Li_2CuO_2. These measurements probe O $2p_x$ (**E**∥**a**), O $2p_y$ (**E**∥**b**), and O $2p_z$ (**E**∥**c**) unoccupied states. The unoccupied states in the ''high'' energy range above 530.5 eV result from the hybridization of Li $2s/2p$ states with previously occupied O bands. We will mainly concentrate on the peak directly above the absorption onset at ~ 530 eV, which is related to transitions into O $2p$ orbitals hybridized with Cu $3d$ states forming the UHB.[12] The polarization dependence is expected to be similar to that found for the white line in the Cu $2p$ absorption spectra. Indeed, in the out-of-plane geometry (**E**∥**c**) the spectral weight of the UHB is strongly suppressed, with less than $\sim 11\%$ of the holes with O $2p$ character located in orbitals perpendicular to the (**a**,**b**) plane. From the observed anisotropy in the Cu $2p$ and O $1s$ absorption edges one can conclude that the UHB is
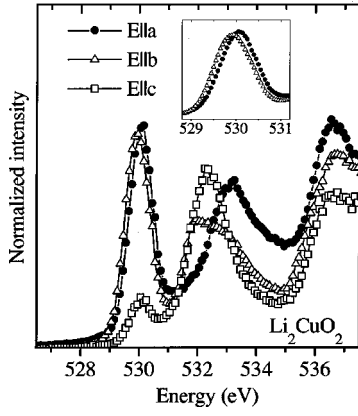
FIG. 3. O 1s absorption edges of Li$_2$CuO$_2$ for the electric-field vector **E** parallel to the three crystallographic axes. The inset concentrates on the upper Hubbard band derived features for the two in-plane light polarizations measured with smaller step size.

predominantly built up from the in-plane orbitals Cu $3d_{xy}$, O $2p_x$, and O $2p_y$. A similar result is found within our LDA approach, in which states other than these three contribute jointly less than 1% to the band at the Fermi level. Compared to the LDA result, the larger out-of-plane contributions observed in experiment are most likely a result of the finite degree of linear polarization ($>90\%$) of the monochromatized synchrotron radiation. Although the relevant orbitals for the formation of the UHB have almost exclusively in-plane character, the LDA band-structure shows a dispersion of the corresponding antibonding band in the z direction which is equivalent to the dispersion in y direction and comparable to that in chain direction x.[18] From this we can conclude that there is a relatively large interchain coupling via oxygen orbitals, and that Li$_2$CuO$_2$ is not an ideal 1D model system as the crystal structure might suggest at the first glance. From the dispersion of the antibonding band of an effective one-band model in chain direction,

$$E(\vec{k}) = -2t_1 \cos(k_x a) - 2t_2 \cos(k_x a)$$
$$-8t'_1 \cos\left(k_x \frac{a}{2}\right)\cos\left(k_y \frac{b}{2}\right)\cos\left(k_z \frac{c}{2}\right)$$
$$-8t'_2 \cos\left(k_x \frac{3}{2}a\right)\cos\left(k_y \frac{3}{2}b\right)\cos\left(k_z \frac{3}{2}c\right), \quad (1)$$

where $t_{1,2}$ denote the intrachain transfer integrals and $t'_{1,2}$ the corresponding interchain integrals, we estimate for the transfer integrals values of $t_1 = -30$ meV (-63 meV), $t_2 = -80$ meV (-94 meV), $t'_1 = -12$ meV (-16 meV), $t'_2 = -44$ meV (-44 meV). The numbers in parantheses are the results obtained by Weht and Pickett.[19] The nearest-neighbor intrachain transfer integral is significantly smaller than the corresponding value of the corner-sharing chain in Sr$_2$CuO$_3$ [0.55 eV (Ref. 20)], reflecting the hindered hopping along the chain direction due to the $\sim 90°$ Cu-O-Cu geometry in Li$_2$CuO$_2$.

We will now focus on the O 1s absorption edges for **E**$\|$**a** and **E**$\|$**b** near 530 eV, where the chain geometry would suggest the expectation of identical spectra. As illustrated in Fig. 1(a), the alignment of the light polarization parallel to the **a**

axis is identical to the situation of **E**$\|$**b** as far as the projection of the unoccupied O $2p_{x'}/2p_{y'}$ states along these two directions is concerned. Surprisingly, in our XAS measurements the UHB derived feature for **E**$\|$**a** and **E**$\|$**b** turn out not to be identical. The hole density in the orbitals O $2p_x$ and O $2p_y$ is almost the same, but we observe a distinct shift in energy of 150 meV between the two polarization directions. Although an absolute energy calibration can hardly be performed to an accuracy of 0.1 eV, we can very sensitively and significantly determine a relative shift between the **E**$\|$**a** and **E**$\|$**b** spectra by adopting the following scheme: the corresponding directions have been measured immediately one after another in a cycle **E**$\|$**a**, **E**$\|$**b**, **E**$\|$**a**. After a new fill of the storage ring, the measurements were repeated but now starting the cycle with **E**$\|$**b**. Thus a jump in the monochromator energy due to the mechanical drive of the grating and/or instabilities of the electron beam in the storage ring can be excluded as an explanation of the shift. Moreover, measurements were performed on several samples with identical results.

To discuss a possible anisotropy between the **a** and **b** direction we make use of the orbital representation shown in Fig. 1(b), which corresponds to the experimental geometry probing O $2p_x$ and O $2p_y$ states. The Cu ions still have an isotropic neighborhood consistent with the observations in the Cu 2p XAS, but now the O $2p_x$ and O $2p_y$ orbitals are not *a priori* symmetrically equivalent. For example, the presence of counterions strongly hybridized with the O $2p_y$ orbitals would lead to a sizeable anisotropy. The crystal structure of GeCuO$_3$ is a good illustration for this situation, as the Ge ions are located directly opposite the oxygen atoms of the edge-sharing chain. In Li$_2$CuO$_2$, however, the Li ions do not reside opposite to the oxygen atoms, but are situated in between them with a O-Li-O bonding angle of approximately $90°$. Thus in the present case the counterions do not give a basis for a possible anisotropy.

In contrast to the corner-sharing chain in Sr$_2$CuO$_3$, where one can naturally ascribe two different peak positions to two symmetrically inequivalent oxygen sites,[2] the crystal symmetry in Li$_2$CuO$_2$ shows only one oxygen site. As the excitation into the two oxygen orbitals starts from the *same* core level, one would consequently expect to observe *one* UHB at a certain energy, provided that possible excitonic effects between the excited electron and the core hole do not depend on the final state (O $2p_x$, O $2p_y$).

In a first step we look for an explanation of the observed energy shift in the framework of the LDA calculation where the partial, orbital resolved unoccupied DOS near the Fermi energy is expected to be reflected in our XAS data directly above the absorption threshold. The character of the orbitals building a dispersive band may change across the Brillouin zone, e.g., from predominantly O $2p_x$ to O $2p_y$. Integrating over k space in the XAS experiment one would then observe a different energy position when probing O $2p_x$ and O $2p_y$ orbitals, reaching in one case mainly the upper part of the band and in the other case mainly the lower part of the band, respectively. Indeed some effect is visible in the O $2p$ net density of states derived from our LDA band-structure calculations shown in Fig. 4. In the lower part of the figure, the calculated DOS has been broadend to account for lifetime effects of the core hole (0.2 eV Lorentzian) and energy reso-
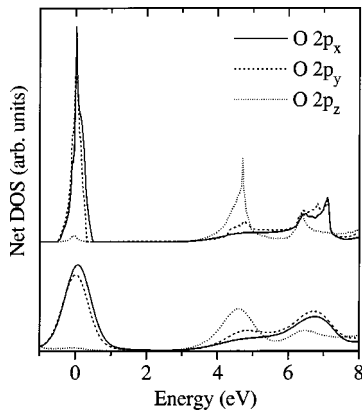
FIG. 4. O $2p$ net density of states of the LDA linear-combination of atomic orbitals band structure near the Fermi energy ($E_F = 0$). Upper curves: calculated DOS. Lower curves: calculated DOS broadened to account for lifetime effects, phonons, and experimental resolution. For the parameters used, see the text.

lution (0.28 eV Gaussian). To reproduce the experimentally observed linewidth of ≈ 1 eV full width at half maximum, an additional broadening of 0.6 eV (Gaussian) has been applied. The origin of this broadening is most likely related to phonons, whereby both the observed practically symmetric lineshape and the large width indicate that we are in the strong coupling limit. One recognizes a small energetic shift between the calculated O $2p_x$ and O $2p_y$ density of states at the Fermi energy, in the same direction as experimentally observed. However, the theoretically estimated shift of 50 meV turns out to be not sufficient to fully explain the experimental value of 150 meV. Therefore, there must be some additional mechanism involved.

As the phonon contributions have significant influence on the actual linewidth, the chain structure of Li_2CuO_2 could lead one to expect some anisotropy of the phonon properties, thus accounting for the experimentally observed energy shift. For example, O $1s$ core-level excitations into the O $2p_x$ and O $2p_y$ orbitals could result in coupling either to differing numbers of phonons or to phonons of differing energies. However, considering the role of phonons in the excitation process in terms of a simple Einstein model, one finds that the first moment (center of gravity) of the spectral function is independent of the coupling strength.[21,22] For an asymmetric lineshape, an energy shift between the two polarization directions could result from the different energy positions of the peak maximum with respect to the center of gravity in each case. However, as the peak maximum and the center of gravity coincides in the strong coupling limit (symmetric lineshape), it would appear unlikely that, within this simple

framework, the observed energy shift is caused by phonon contributions. We cannot, however, exclude that a much more sophisticated theoretical model involving strong anharmonicity could account in part for the energy shift. Such a complex and technically difficult treatment is clearly beyond the scope of the present paper.

As a final point we mention the possible role played by electronic correlation effects in the XAS final state. Since there are only 0.1 holes per O $2p_{x,y}$ orbital, the excited electron must be distributed over several surrounding ions. This charge redistribution in the XAS final state depends sensitively on the transfer integrals between the orbitals involved. These are in turn influenced by geometric effects (the Cu-O-Cu bond angle is 94°) and in the case of the oxygen-oxygen transfer integrals additionally by the proximity of cations in the immediate vicinity. Both of these effects could lead to a situation in which the final state charge distribution is different for the two polarization conditions. Taking this fact, in combination with the various intersite Coulomb interactions (both core-valence and valence-valence), it is conceivable that the final state energies for $\mathbf{E} \parallel \mathbf{a}$ and $\mathbf{E} \parallel \mathbf{b}$ result in a shift of both the same magnitude and direction as observed in experiment. Consequently, the direction and magnitude of the experimentally observed energy shift provide useful constraints for the parameters involved in future model calculations of edge-sharing CuO_2 chains.

To summarize our results, direct experimental information on the character and symmetry of the intrinsic holes in the edge-sharing chain of Li_2CuO_2 has been obtained by polarization-dependent x-ray absorption spectroscopy. Although for light polarization within the plane of the CuO_4 plaquettes the chain geometry suggests isotropic oxygen contributions to the UHB, we observe a shift in energy in dependence of the direction of the light polarization. This shift has been discussed within the framework of band-structure effects, the role of phonons in the excitation process, as well as the impact of electronic correlations in the XAS final state.

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