The unusual electronic structure of the "pseudo-ladder" compound CaCu$_2$O$_3$

T.K. Kim, H. Rosner, S.-L. Drechsler, Z. Hu, C. Sekar, G. Krabbes, J. Málek, M. Knupfer, J. Fink, H. Eschrig
Leibniz-Institute for Solid State and Materials Research Dresden, P.O.Box 270116, D-01171 Dresden, Germany
1 Department of Physics, University of California, Davis, CA 95616, USA

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Experimental and theoretical studies of the unoccupied electronic structure of CaCu$_2$O$_3$ single crystals have been performed using polarization-dependent x-ray absorption spectroscopy and band structure calculations. The measured hole distribution shows an unusual large number of holes in orbitals parallel to the interlayer direction which is in agreement with the theoretical analysis. CaCu$_2$O$_3$ deviates significantly from the standard $p$_d cuprate picture. The corresponding strong interlayer exchange is responsible for the missing spin gap generic for other two-leg ladder cuprates.

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The electronic structure and magnetic properties of cuprates exhibiting various interesting physical properties have been intensively studied in recent years. In particular, considerable attention has been attracted by so-called spin-ladders. Their study might contribute to a complete understanding of spin and charge excitations in high-\(T_c\) superconductors since in the presence of a spin gap \(d\)-wave superconductivity might occur in spin-ladder compounds. Superconductivity under high pressure has been reported in \(\text{Sr}_1.4\text{Cu}_2\text{O}_{41}\) and \(\text{CaCu}_2\text{O}_{3}\). So far, only a few studies were carried out for \(\text{CaCu}_2\text{O}_3\) (belonging structurally to the ladder family; see Fig. 1). However, the magnetic susceptibility \(\chi(T)\) is quite different from that of the prototype two-leg ladder system \(\text{SrCu}_2\text{O}_3\). From \(\chi(T)\) an antiferomagnetic ordering below a Néel temperature \(T_N\approx25\) \(\text{K}\) was concluded. In order to contribute to the understanding of ladder compounds in general and to clarify the character of the hole distribution in \(\text{CaCu}_2\text{O}_3\), polarization dependent x-ray absorption spectroscopy (XAS) studies of single crystalline samples were performed. We report the experimentally studied unoccupied electronic structure together with that derived from band structure calculations within the local density approximation (LDA) and show that at variance with usual ladder compounds, the hole distribution in \(\text{CaCu}_2\text{O}_3\) has a strong non-planar nature.

The \(\text{CaCu}_2\text{O}_3\) single crystals were grown by the traveling solvent floating zone (TSFZ) method. The as grown crystals were found to be phase pure as confirmed by X-ray diffraction, energy dispersive X-ray (EDX) and thermogravimetric analyses. Further, the EDX results indicate a deficiency of \(\text{Ca}\) with a balancing excess in \(\text{Cu}\) corresponding to a nonstoichiometric composition \(\text{Ca}_{0.86}\text{Cu}_{1.4}\text{O}_{2.93}\) in agreement with the structure refinement by Ruck et al. The lattice constants were determined to be \(a = 9.946\) Å, \(b = 4.079\) Å and \(c = 3.460\) Å in agreement with the values found in the literature.

Single crystal samples with the size of \(\approx 5\times5\times2\) mm$^3$ were cut from the grown rod for the XAS measurements. The determination of the sample orientation was carried out by taking Laue-images (image plate), followed by a simulation of the surface orientation. The structure of this material, shown in Fig. 1, is similar to that of \(\text{SrCu}_2\text{O}_3\). It consists of an array of ladder-like structures with quasi-one-dimensional copper-oxide chains extending along the crystallographic \(b\) direction. However, while in the Sr compound the Cu-O-Cu bond angle in the rungs is \(180^\circ\), in \(\text{CaCu}_2\text{O}_3\) it turns out to be \(\approx 123^\circ\).

The XAS experiments were carried out using linearly polarized light from the U49/1-PGM beam-line at the synchrotron light source BESSY II in Berlin. The energy resolution of the monochromator was set to be 280 and 660 meV at the O $1s$ and Cu $2p$ absorption thresholds, respectively. A core-level excitation whose absorption coefficient is small compared to the total absorption, as in the case for the O $1s$ edge, leads to a very poor signal-to-background ratio in total electron yield (TEY), but has the distinct advantage that self absorption effects in the fluorescence yield (FY) mode remain small. The situation is just reversed in the case of the relatively strong Cu $2p$ absorption. Therefore, for the O $1s$ and the Cu $2p$ absorption spectra we chose the FY

FIG. 1: The crystal structure of \(\text{CaCu}_2\text{O}_3\). The corner-shared \(\text{CuO}_2\) zigzag chains running along the \(b\)-axis are alternatingly tilted by nearly $28.55^\circ$ forming positively and negatively buckled ladders with “kinked” rungs in \(a\)-direction.
The polarization dependent measurements probe mainly the hole distribution in the Cu 3d states located in the O 2p and Ca states, is more pronounced. As for the Cu 2p edge, for the O 1s absorption a relatively big fraction of holes was found in c direction compared to the “one-leg ladder” compound SrCuO$_2$ and the two-leg-ladder Sr$_{14}$Cu$_{24}$O$_{41}$. This unusual behavior will be discussed below together with LDA results.

In order to get insight into the projected density of states in the different directions, band structure calculations were performed using the full-potential nonorthogonal local-orbital minimum-basis scheme \[16\] within the LDA. In the scalar relativistic calculations we used the exchange and correlation potential of Perdew and Zunger \[20\]. Cu (3s, 3p, 4s, 4p, 3d), O(2s, 2p, 3d), and Ca (3s, 3p, 4s, 4p, 3d) states, respectively, were chosen as the basis set. All lower lying states were treated as core states. The inclusion of Cu and Ca (3s, 3p) states in the valence states was necessary to account for non-negligible core-core overlaps. The O 3d states were taken into account to increase the completeness of the basis set. The spatial extension of the basis orbitals, controlled by a confining potential \[21\] \((r/r_0)^3\), was optimized to minimize the total energy. The results of the paramagnetic calculation (see Fig. 2) show a valence band complex of \(\approx 8\) eV width with four bands crossing the Fermi level \((E_F=0)\) according to the four copper atoms per unit cell. An analysis of partial densities of states (not shown) shows that the valence band is mainly built by Cu 3d and O 2p states with small contributions of Cu 4s and 4p states at the bottom of the valence band due to hybridization. The contribution of Ca states is negligible.

The two band complexes at \(E_F\) (see Fig. 2) have the typical bandwidth of CuO$_2$-chain derived compounds of \(\approx 2\) eV and are nearly half-filled \[28\]. Furthermore, strong correlation effects are present which explain the experimentally observed insulating ground state. As one would expect, the main dispersion of these two antibonding Cu 3d-O 2p band complexes (with respect to the Cu-O bonds) occurs along the Γ-Y direction, corresponding

![FIG. 2: Polarization dependent XAS spectra at the (a) Cu 2p and (b) O 1s absorption edges of CaCu$_2$O$_3$.](image)
to the crystallographic $b$ direction of the CuO$_2$ double chains (legs). The upper band along (Γ-X, X-S, S-Y, U-R, R-T, and the group with stronger dispersion along Γ-Y is antibonding in nature whereas their counter part is bonding (now with respect to the rung Cu-Cu bond of the ladder). They are split by about 0.5 eV due to the interactions $t_\perp$ via the rung. The weak interladder coupling causes a further small splitting along the Γ-X, Γ-Y, Γ-Z and Z-U lines. Within the corresponding zigzag representation the shift of the neighboring leg by $b/2$ in real space results in a doubling of the Brillouin zone (BZ) along the $b$-axis: $(-2\pi/b \leq k_y \leq 2\pi/b)$. Then that secondary splitting can be understood as a band defolding in the original twice as short BZ. Surprisingly, the “interlayer” dispersions along Γ-Z (crystallographically || to c) are quite strong for a cuprate compound being of the same order as that along the rungs as mentioned above, i.e. of the order of $\sim$ 500 meV. For the bonding bands the 2$p_z$, O(1) orbitals involved due to the strong buckling (which produce there locally odd parity (under reflection along the c-axis) of the corresponding “molecular” rung orbitals) cause negative dispersion along Γ-Z. Contrary the usual positive cosine-like dispersion of the antibonding band is caused by predominant Cu 3$d$ contributions with even parity and a much smaller admixture of O 2$p_z$ states. The dispersion along $a$ is rather small due to the weak coupling between the sub-chains of the double (zigzag) chain (shaded structural blocks in Fig. 1). The reason for the weak inter-sub-chain coupling is the nearly 90° Cu-O-Cu bond between neighboring Cu in different sub-chains. The relative number of holes in the O2$p$ and Cu 3$d$ orbitals pointing along the respective crystal directions can be derived from the intensity of the lowest lying absorption feature in the O 1$s$ and Cu 2$p$ absorption edges, respectively. These numbers are listed in Table I and compared to those obtained for the projected density of states form our band structure calculations.

Table I demonstrates that the XAS and the theoretically derived numbers are in good agreement. Both reveal that about 40% of the holes occupy orbitals along the $a$ and $b$ directions. Strikingly, a relatively big portion ($\approx$ 20%) of holes is found in orbitals along the $c$ direction. At first glance this anomalous large number of non-planar holes as compared to the “normal ladder” could be understood considering simply projections due to the buckled structure of CaCu$_2$O$_3$. From the measured relative O hole number 0.37 in $a$-direction one has a local “in-plane (plaatquette) of 0.37/cos$^2$$\theta$ = 0.48 nominal hole concentration, where $\theta \approx \pm 28.55°$ is the local tilting angle (see Fig. 1). Projecting this number on the $c$-axis, a contribution of only 0.11 nominal O holes would be expected in contrast with the observed 0.27 nominal ones. Hence, there are about 0.16 nominal holes from orbitals which usually do not enter the ground state of a local Cu-O hole distribution ratio with 2.4 Cu and 1.6 O holes per unit cell. Then one has $\approx$ 0.26 absolute holes residing in nonstandard plaatquette O 2$p$ orbitals. Within the LDA one arrives at $\approx$ 0.104 nominal “anomalous” O 2$p_z$ holes which reside mostly (71%) in the O(1) 2$p_z$ states on the rung. Remarkably, just these states yield an important contribution to the coupling in $c$-direction as discussed above for the bonding band. While the Cu-O(1)-Cu bond angle (180° – $2\theta$) at the rungs decreases from 180°, as it would be in the case of a “normal” planar ladder (e.g. SrCu$_2$O$_3$), the coupling of the electronic states of two legs within the ladder through the rung oxygen is reduced, and above some critical angle $\theta = 45° - \delta$ in approaching the almost “decoupled” chain limit at 45° it might become even smaller than that in $c$ direction. Considering the Cu holes, we arrive at $\approx$ 0.12(0.3) anomalous nominal (absolute) holes. Thus in total $\approx$ 0.56 (Cu + O) anomalous holes of 4 holes per unit cell are moved into $c$-axis oriented orbitals. This is much more than usually observed in various planar cuprates (< 0.05 holes per Cu which is mainly attributed to the experimentally available slightly nonideal polarization in the present day XAS experiments; see e.g. Refs. [18, 22]). This clear effect then also leads to more isotropic spin interactions for CaCu$_2$O$_3$ which is consistent with the observation of a 3D Néel like transition at $T_N$ = 25 K in magnetic susceptibility measurements [18, 19], while SrCu$_2$O$_3$ stays in the spin gaped nonmagnetic state down to $T = 0$. As our LDA-results point to a comparable rung and interlayer hopping integral $t_\perp$ $\sim$ 250 meV and $t_z$ $\approx$ ± 125

**Table I: Relative number of holes for different polarization directions from XAS experiment and LDA calculations.**

| $n_h$, % | a  | b  | c  |
|--------|----|----|----|
| O$_{theory}$ | 35 | 44 | 21 |
| O$_{exp}$   | 37 | 36 | 27 |
| Cu$_{theory}$ | 47 | 36 | 17 |
| Cu$_{exp}$  | 36 | 41 | 23 |
meV, comparable antiferromagnetic exchange integrals $J_1 \sim 50$ meV and $J_2 \sim 20$ meV within a simple bilinear spin-1/2 Heisenberg model picture can be expected.

The consideration of a ferromagnetic contribution of the same order as $J_z$ due to Hund’s rule coupling between O(1) $2p_x$ and $2p_z$ orbitals introduced by the rung buckling,[23] would bring both exchange integrals still closer to each other. Then, the critical regime expected near $J_z \sim 0.3 \sqrt{J_0/J_{\perp}}$ is arrived (compare Ref. [26]). In this way, the standard ladder picture becomes invalid and we arrive at a picture of coupled ordered chains whose ground state is a Néel-like state (period doubling along $b$- and $c$-directions but an incommensurate ordering in $a$-direction due to the frustrated ladder arrangement).

The numbers given above should be compared with those of the spin gaped planar ladder compound SrCu$_2$O$_3$[3] where at a comparable large $J_{\parallel} \approx 130$ to 150 meV, a larger $J_\perp \approx 72$ meV has been found. But most importantly, only a tiny $J_z \sim 1$ meV can be expected.[27] Thus, CaCu$_2$O$_3$ is only a “pseudo-ladder” compound which differs markedly from standard two-leg ladders. Since the interladder exchange along $a$ is weak, we arrive at a picture which is essentially in line with that put forward by Kiryukhin et al.[6] who suggested that CaCu$_2$O$_3$ can be described as an array of 2D “$b$-$c$ double-planes” in which spins-1/2 are coupled by spatially anisotropic antiferromagnetic exchange interactions described by the isotropic (in spin space) Heisenberg model.

In conclusion, we have studied the unoccupied electronic structure of the “pseudo-ladder” compound CaCu$_2$O$_3$. The experimental XAS data of the relative hole numbers is in good agreement with the LDA values. Further calculations to study correlation and impurity effects are necessary to address some remaining small deviations. At variance with the normal ladder picture (and more generally also with all other known cuprates comprised from isolated or shared CuO$_4$-plaquettes in straight or planar networks) the hole distribution has a less pronounced local O2pCu$d$($\sigma$ character. Here it is related to the missing spin gap and the antiferromagnetically ordered Néel-like state below 25 K. A broad study of the properties of this unique cuprate, including doping, is of interest for the ladder and the cuprate physics in general. In particular, any doping induced superconductivity would be different from the spin-gap based scenario proposed for two-leg ladder cuprates.

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[**] Present address: II. Physikal. Inst., Universität zu Köln, Zülpicher Str. 77, D-50937 Köln, Germany.

[1] T. M. Rice et al., Europhys. Lett. 23, 445 (1993).
[2] E. Dagotto, Rep. Progr. Physics 62, 1525 (1999).
[3] T. F. A. Müller et al., Phys. Rev. B 57, R12 655 (1998).
[4] M. Uehara et al., J. Phys. Soc. Jpn. 65, 2764 (1996).
[5] M. Isobe et al., Phys. Rev. B 57, 613 (1998).
[6] V. Kiryukhin et al., Phys. Rev. B 63, 1444418 (2001).
[7] K. Ruck et al., Mat. Res. Bull. 36, 1995 (2001).
[8] M. Azuma et al., Phys. Rev. Lett. 73, 3463 (1994).
[9] C. Sekar et al., Physica C (accepted for publication).
[10] Christ. Teske et al., Z. Anorg. Allg. Chem. 370, 135 (1969); R. Arpe et al., ibid. 426, 1 (1976).
[11] Z. Hiroi et al., J. Solid State Chem. 95, 230 (1991).
[12] H. Petersen, et al., Rev. Sci. Instrum. 66, 1 (1995); C. Jung et al., SPIE 3150, 148 (1997).
[13] N. Nücker et al., Z. Phys. B 67, 9 (1987).
[14] L. Tröger et al., Phys. Rev. B 46, 3283 (1992).
[15] Transitions into unoccupied Cu 4$s$ states are also allowed, but show a reduced transition probability by a factor of 20 compared to Cu 3$d$ final states: B.K. Teo and P.A. Lee, J. Am. Chem. Soc. 101, 2815 (1979).
[16] J. Fink et al., J. Electrosc. Spec. Relat. Phen. 66, 395 (1994).
[17] M. Knupfer et al., Phys. Rev. B 55, R7291 (1997).
[18] N. Nücker et al., Phys. Rev. B 62, 14 384 (2000).
[19] K. Koepernik et al., Phys. Rev. B 59, 1743 (1999).
[20] J. P. Perdew et al., Phys. Rev. B 23, 5048 (1981).
[21] H. Eschrig, Optimized LCAO Method and the Electronic Structure of Extended Systems (Springer, Berlin, 1989).
[22] R. Neudert et al., Phys. Rev. B 62, 10752 (2000).
[23] A more sophisticated mapping including also cyclic four-spin and anisotropic two-spin interactions,[24][25] both are affected by the buckling, is left for future work.
[24] S. Brehmer et al., Phys. Rev. B 60, 329 (1999).
[25] R. Citro and E. Orignac, Phys. Rev. B 65, 134413 (2002).
[26] L. Capriotti et al., Phys. Rev. B 65, 092406 (2002), showed that for coupled isotropic ladders ($J = J_\perp = J_z$) at $T = 0$ a quantum phase transition from a spin gap to a Néel phase occurs near strong interladder (IL) coupling $J_{IL} = 0.3J$.
[27] As it also has been estimated for the strongest interchain exchange in the closely related single chain compound Sr$_2$Cu$_2$O$_3$[24] this value rises to about 3 to 4 meV for the isomorph Ca$_2$Cu$_2$O$_3$ due to the reduced interchain distance[28] which is of interest in the present context.
[28] H. Rosner et al., Phys. Rev. B 56, 3402 (1997).
[29] The value of this ferromagnetic contribution depends on the onsite energy difference between the two involved O 2$p$ orbitals, the direct ferromagnetic exchange interaction between O and Cu orbitals, as well as on the Cu-O(1)-Cu bond angle. To estimate the total ferromagnetic contribution, we mention that in CuGeO$_3$ with a nearly 99° Cu-O-Cu bond angle it amounts to $\approx 15$ meV.[29] In the corner-shared BaCu$_2$Si$_2$O$_7$ with a Cu-O-Cu bond angle of 124° very close to our case, a total exchange integral of 24 meV has been estimated,[28] which is in accord with our estimate given above.
[30] H. Rosner et al., Phys. Rev. B 63, 073104 (2001).
[31] M. Poirer et al., Phys. Rev. B 66, 054402 (2002).