The hole distribution in cuprate chains

**S.-L. Drechsler, J. Málek, H. Rosner,
R. Neudert, M. Knupfer, M.S. Golden, J. Fink, H. Eschrig,
C. Waidacher†, R. Hetzel†**

Institut für Festkörper- und Werkstofforschung Dresden, Postfach 270016, D-01171 Dresden, Germany
† *Institut für Theoretische Physik, Technische Universität Dresden, Germany*

The electronic structure of the prototypical corner-sharing Sr_2CuO_3 *linear chain compound is investigated by combining several theoretical and experimental techniques. Band structure calculations within the local density approximation and using a local orbital basis provided the relevant orbitals and the transfer integrals for a four-band extended Hubbard pd-model, which was treated by means of exact diagonalization and of quantum Monte Carlo calculations for finite chain clusters. The band structure values of the transfer integrals* t_{pd} *exceed the corresponding values for layered cuprates. Enhanced values of the intersite Coulomb interaction,* V_{pd} *= 2 ... 2.5 eV, and a difference between the onsite energies of side and chain oxygen* Δ_{pp} *= 0.5 ... 0.75 eV are deduced from the comparison of the model studies with the intensities of polarization dependent x-ray absorption spectra. The latter reflect the hole distribution over the oxygen sites.*

1. INTRODUCTION

Corner- and edge-sharing linear cuprate chains are important building blocks of the more complex zigzag chains in $SrCuO_2$, of various ladders, and related compounds. Sr_2CuO_3 and Li_2CuO_2 with undoped chains are the parent compounds for an increasing number of doped chain compounds. The latter cannot be described quantitatively before the parent compounds are well understood. However, even for these, structurally and physically much simpler, undoped parent compounds there are several unsettled problems such as the origin of the very large value of the in chain exchange integral $J_\parallel \approx 200$ to 260 meV. These problems also cannot be attacked without knowledge of the relevant parameter set, which presumably differs from that of the layered cuprates. It is our aim to contribute to the understanding of these challenging systems and to find out to which interactions the polarization dependent x-ray absorption spectroscopy (XAS) is most sensitive. We hope that combining theoretical analysis and various spectroscopies, the main parameter values of the extended Hubbard model of the various chain cuprates can be found.

2. ELECTRONIC STRUCTURE

In order to find reliable estimates for the mentioned above transfer integrals, we analyzed at first the orbital character of the bandstructure of Sr_2CuO_3 near the Fermi energy E_F.[1] At first glance only the half-filled antibonding band near E_F needs to be considered. However, the extended tight-binding fit for this band is numerically unstable, and the three different values of transfer integrals required in the four-band *pd* model cannot be determined from this band alone (See Fig. 1 and Eq. (1) for our notation of axes, sites, and parameters.). Thus, we were forced to include also additional energetically lower lying bands which have bonding and nonbonding character. But due to the non-negligible hybridization with further O $2p$ orbitals, within the four band model, a discontinuity of the O(2) $2p_y$ character is observed in the region of the nonbonding O(2) derived bands near -4 and -5 eV (see Fig. 2, left panel).

Therefore finally, a fit was performed within the seven-band *pd*-model where the O(1) $2p_y$, two O(2) $2p_x$-orbitals were additionally taken into account although they can be widely ignored in the low-energy physics described below. To illustrate the improvement of the seven-band fit with respect to reasonably small second neighbor transfer t_{pp}, we list the obtained transfer integrals: t_{p1d}=1.57eV, t_{p2d}=1.8eV, t_{p1xp2y}=0.62eV, t_{p1yp2x}=0.41eV, t_{p1xp2x}=t_{p1yp2y}=0.4eV, to be compared with t_{p1d}=1.45eV, t_{p2d}=1.8eV, t_{pp}=1.15eV (!), of the four-band fit. Thus an extended fit with a subsequent selection of relevant orbitals is better than a more restricted one with uncontrolled neglect of other orbitals. In this context we mention that the small admixture of Cu $4s$ and O $2s$ states contributes also

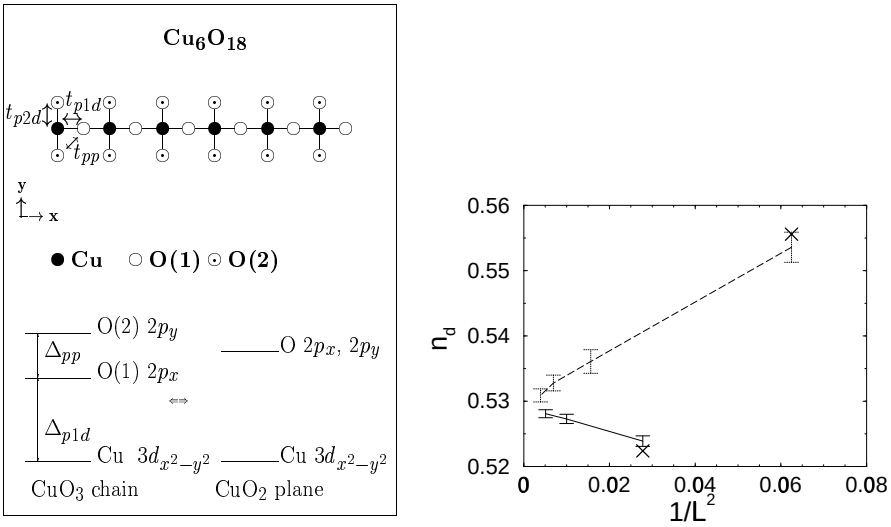

Fig. 1. **Left panel**: Typical $(CuO_3)_L$ $L = 6$ cluster with periodic boundary conditions used in the EDS reported below. The notation of sites, orbitals, and corresponding one-particle Hamiltonian parameters used within our EDS approach are given. **Right panel:** Size effect for the Cu hole occupation number n_d calculated within the Quantum Monte Carlo method. The crosses denote our EDS results.

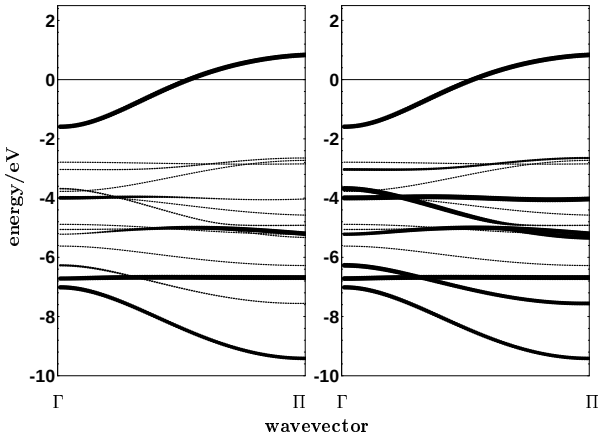

Fig. 2. Band structure of Sr_2CuO_3 along the chain direction. The thickness of the lines scales with the orbital weight of the 4-band (**left panel**) and of the 7-band model (**right panel**).

somewhat to the relatively large width of the antibonding band.

3. EXACT DIAGONALIZATION STUDIES (EDS)

According to the orbital analysis (see Sec. 2) three main orbitals contribute more than 94 % to the total density of states of the antibonding band, namely the O $2p_x$ and O $2p_y$ as well as the Cu $3d_{x^2-y^2}$ states. Hence, the usual *pd*-model with one orbital per site but extended to two nonequivalent oxygen sites per unit cell is a good first approximation and we arrive at a four-band extended Hubbard model (see e.g. Ref. 3) supplemented here with the core hole - valence hole Coulomb interactions in the x-ray absorption (XAS) final state:

$$\begin{aligned} H &= \sum_i \varepsilon_i \hat{n}_i + \sum_{<i,j>,s} t_{ij}(c^\dagger_{i,s} c_{j,s} + h.c.) + \sum_i U_i \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} \\ &\quad + \sum_{<i,j>} V_{ij}\hat{n}_i\hat{n_j}i + \sum_i U_{ci}\hat{n_{ci}}\hat{n_i} + \sum_{<i,j>} V_{ci}\hat{n_{ci}}\hat{n_j}\,. \end{aligned} \tag{1}$$

$c^\dagger_{i,s}$ creates a hole with spin projection s at site i, $\hat{n}_{i,s} = c^\dagger_{is} c_{is}$ is the occupation number operator, and $\hat{n}_i = \sum_s c^\dagger_{is} c_{is}$. In the following we shall denote the difference of O(1) $2p_x$ and Cu $3d_{x^2-y^2}$ onsite energies by Δ_{pd} and the corresponding difference of O(2) $2p_y$ and O(1) $2p_x$ energies by Δ_{pp} (see Fig. 1, right panel). For the onsite Coulomb repulsion at Cu and O sites we adopt $U_d = 2U_p$=8.8 eV, respectively, as suggested in Ref. 4. For the intersite Coulomb interactions we adopt for the sake of simplicity $V_{p1d} = V_{p2d} = V_{pd}$. Then the latter value as well as the value of Δ_{pp} are taken as free parameters to reproduce the XAS data reported below. We have calculated the XAS spectral function as well as the hole occupation numbers,

$$n_i = < G \mid \hat{n}_i \mid G >, \tag{2}$$

in the ground state $\mid G >$ on Cu, n_d, and on both oxygen sites O(1) and O(2), since the measured polarized O $1s$ XAS cross sections are proportional to the oxygen occupation numbers in the ground state. In order to get some insight in the finite size effects caused by the small clusters which can be treated by EDS, we compared our findings with those of Quantum Monte Carlo calculations, where up to 16 unit cells can be considered (see Fig. 1, left panel). First of all the $1/L^2$ asymptotic behaviour on *different* curves for L=$4m$ and L=$4m$+2 (m=0,1,...) clusters should be mentioned. Since the deviations at small L are very small ~ 0.4 %, we regard the result for L=16 as an excellent estimate for the $L \to \infty$ limit. The results for any quantity calculated at $L = 6$ and $L = 4$ cluster sizes can be regarded as lower and upper bounds for the infinite chain limit of interest. As an estimate we arrive for instance at $n_d(6) < n_d(\infty) \approx 0.8 n_d(6) + 0.2 n_d(4) < n_d(4)$.

4. COMPARISON WITH XAS EXPERIMENTAL RESULTS

The experimentally measured O $1s$ spectra with the electric field parallel and perpendicular to the CuO_3 chain axis is shown in Fig. 3. Notice the shift of about 0.5 eV between the two directions for the two peaks just above the threshold at 528 eV. ¿From the integrated spectral weight near the peaks the value of the oxygen hole ratio $R = 2n_{O(2)}/n_{O(4)} \approx 1.22$ can be deduced. The shift which scales with V_{cd} and can be reproduced for weak core hole-copper interaction $V_{cd} \approx 0.4$ eV, reflecting the different numbers of Cu neighbors seen by the core hole at the O(1) site and the O(2) site. ¿From the strong intersite interaction V within the one-band extended Hubbard model seen in the EELS data of Ref. 2 we obtain a non-zero value of V_{dd}.

5. DISCUSSION AND CONCLUSION

Based on bandstructure calculations for Sr_2CuO_3 a new parameter set at the level of the four-band extended Hubbard *pd* model description has been proposed. Surprisingly significant deviations from sets commonly accepted for layered cuprates have been found indicating that the t_{pd}, t_{pp}, etc. do not scale with the Cu-O distance. These deviations are considered as the origin of the large values of the intrachain exchange integral. At variance to other spectroscopies the polarization dependent XAS for the anisotropic Sr_2CuO_3 single crystals under consideration is found to be

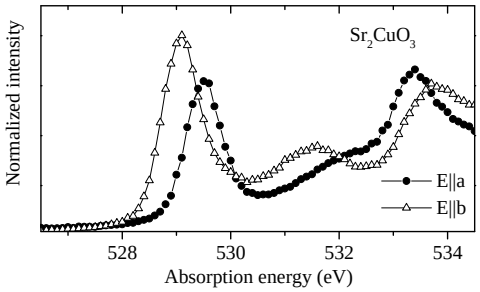

Fig. 3. X-ray absorption spectra of Sr_2CuO_3 for the electric field vector **E** within the plane of the CuO_4 plaquettes. The a-axis corresponds to the chain direction.

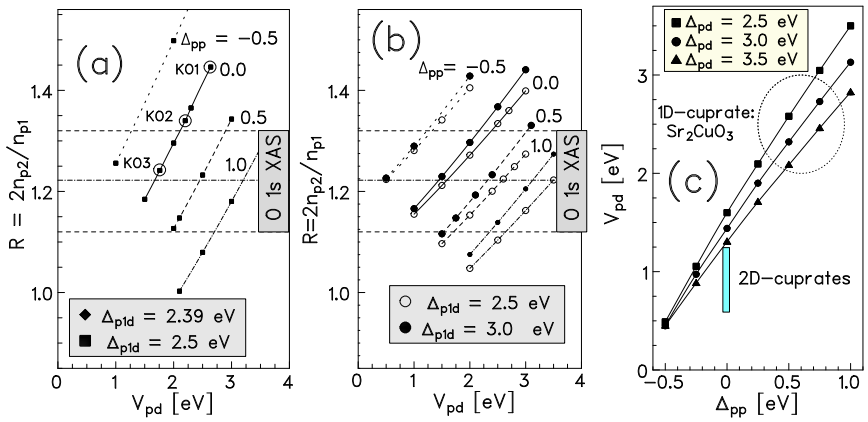

Fig. 4. **(a)** Ratio of O(1) and O(2) occupation numbers *vs.* intersite Coulomb interaction V_{pd} and parameter sets proposed in Ref. 4. The legend numbers denote the difference of oxygen onsite energies Δ_{pp} in eV. The stripe denotes the experimentally (XAS) derived oxygen hole ratio including error bars. **(b)** The same as in (a) for our band structure derived parameter set. **(c)** The correlation between the value of the intersite Coulomb interaction and the oxygen onsite energy difference Δ_{pp} as derived from (b). The large circle denotes the expected region of V_{pd} and Δ_{pp} which should be compared with the narrow box standing for typical layered cuprates.

very sensitive to the difference of onsite energies Δ_{pp} and to the intersite Coulomb interaction V_{pd}. This is demonstrated in Fig. 4 for parameter sets KO1 to KO3 ($t_{p1d} \equiv t_{p2d}$=1.3eV, $\Delta_{pp} \equiv 0$) taken from Ref. 4, our modifications with respect $\Delta_{pp} \neq 0$ (Fig. 4a), and for our band structure derived parameter set (Fig. 4b). From these dependences our main result, the evidence for enlarged intersite Coulomb interactions compared with typical layered cuprates, can be obtained (Fig. 4c).

ACKNOWLEDGMENTS

This research is supported by the DFG under contracts Es 85/6-1, Fi 439/8-1. We thank the group of G. Kaindl, Freie Universität Berlin, for technical assistance.

REFERENCES

1. H. Rosner, *et al.*, *Phys. Rev. B.* **56**, 3402 (1997).
2. R. Neudert *et al.*, *Phys. Rev. Lett.* **81**, 657 (1998), W. Stephan and K. Penc, *Phys. Rev. B* **54**, 17 269 (1998).
3. S.-L. Drechsler *et al.*, *Phys. Rev. B* **53**, 11328 (1996); ibid. **55**, 606 (1997).
4. K. Okada and A. Kotani, *J. Jpn. Phys. Soc.* **66**, 341 (1997).