Journal of Superconductivity, Vol. 10, No. 4, 1997

Electronic Structure and BOW–CDW States of CuO_3 Chains

S.-L. Drechsler,[1] J. Malek,[2] H. Eschrig,[3] H. Rosner,[3] and R. Hayn[3]

Received 30 January 1997

The interplay of structure and bonding is considered for hole-doped anionic cuprate chains and layers. Based on an analysis of available experimental data it is conjectured that the local doping level tends to be close to $\delta = 0$ or $\delta = 0.5$ or $\delta = 1$, where δ is the hole number relative to the Cu $3d$ state, and that $\delta \approx 0.5$ is relevant for superconductivity. Estimates for the strongly anisotropic exchange integrals from LDA band structures for Sr_2CuO_3 and Ca_2CuO_3 are reported. Exact diagonalization studies for undistorted and distorted chain clusters indicate a weakly correlated state in CuO_3 chains doped with 0.5 holes.

KEY WORDS: Cuprate structure; bond order wave; charge density wave.

1. STRUCTURE CHEMISTRY OF CUPRATES

The structural building blocks of all anionic cuprate networks is the $[CuO_4]^{-6\pm\delta}$ plaquette (Fig. 1a). Its excitation spectrum consists of a broad region ($\sim$10 eV) of holes in bonding and nonbonding Cu $3d$–O $2p$ molecular states and a well-separated antibonding dp-σ^* state whose orbital is sketched on Fig. 1a. For $\delta = -1$ the antibonding state is occupied and no binding is obtained. For $\delta \leq +1$ the Cu d level decreases considerably, and the Cu $3d$ and O $2p$ states do not resonate any more. Again the covalent bonding is destroyed.

The total hole count of $[CuO_4]^{-6\pm\delta}$ is $h = 1 + \delta$. One hole resides essentially on the copper site and δ is distributed over all sites, with a preference of the oxygen sites.

The most common chain structure appears to be $[CuO_3]^{-4\pm\delta}$ (Fig. 1b). Now the antibonding states collectivize into a dp-σ^* band of width $\sim$2 eV. As is easily seen from the sign relations of Fig. 1b, the antibonding character forms on the Brillouin zone (BZ) boundary while the Bloch state at the BZ center is nonbonding. The band develops out of the nonbonding hole excitation spectrum as the wave vector increases. For $\delta = 0$ it is half-filled. This is the case of $(Sr_xCa_{1-x})_2CuO_3$, $0 \leq x \leq 1$. In $YBa_2Cu_3O_{7-x}$, which in our systematics should be written as $YBa_2(CuO_2)_2(CuO_3)_{1-x}(CuO_2)'_x$ (the prime indicates the CuO_2 dumbbells), we found by a careful analysis that in the fraction formed by $[CuO_3]^{-4\pm\delta}$ chains $\delta \approx 0.5$ independent of x [1].

Another type of chains is formed of $[CuO_2]^{-2\pm\delta}$ units (Fig. 1c). In this case a dp-σ_1^* state leads to a band antibonding around the BZ center and another dp-σ_2^* state becomes again antibonding around the BZ boundary. In between both hybridize into a narrow ($\leq$1 eV) antibonding band [2]. It is again half-filled ($\delta = 0$) in Li_2CuO_2 and in $(GeO)CuO_2$, but it is unoccupied ($\delta = +1$) in $NaCuO_2$.

Finally, the superconducting cuprate planes are formed of $[CuO_2]^{-2\pm\delta}$ units (Fig. 1d), where now the two-dimensional dp-σ^* band is broader than in the chains. The dp-σ^* band is always split by an appreciable correlation gap for $\delta = 0$, leading to an antiferromagnetic ground state. Density of states develops at the Fermi level in the gap for $\delta \neq 0$. However, there is experimental evidence (e.g., [3,4]) of a stripe superstructure, at least dynamically, in the $[CuO_2]^{-2\pm\delta}$

[1]Institut für Festkörper-und Werkstofforschung IFW Dresden e.V., Germany.
[2]Institute of Physics of AV CR, Prague, Czech Republic.
[3]Max-Planck-Arbeitsgruppe, "Elektronensysteme," Technische Universität Dresden, Germany.

0896-1107/97/0800-0393$12.50/0

planes, so that, if one considers the plane as a stacking of chains, three adjacent chains have $\delta = 0$ and every fourth chain has $\delta \neq 0$ and is nonmagnetic and metallic. The interesting singular case, e.g., in $(La, Ba)_2CuO_4$, is on average $\langle\delta\rangle = 1/8$ which is nonsuperconducting, and which implies $\delta = 0.5$ in the nonmagnetic chains of the stripe structure.

Conjecturing that the stripe structures in $[CuO_2]^{-2\pm\delta}$ planes are generic, we conclude that *in all cuprates either* $\delta \approx 0$, *or* $\delta \approx 0.5$, *or* $\delta \approx 1$. In the vicinity of $\delta = 0$ one finds antiferromagnetic insulators, and *in the vicinity of a "magic" hole doping level of* $\delta = 0.5$ *in chains one finds high-temperature superconductivity*.

Our conclusion implies that the optimum doping case of La_2CuO_4 superconductors, being $\langle\delta\rangle = 1/6$, corresponds to a stacking of two magnetic chains with $\delta = 0$ followed by a nonmagnetic chain with $\delta \approx 0.5$. This is in agreement with the conjecture of Emery *et al.* [5] considering an induced spin gap to be important (which only appears for an even number of chains in the magnetic stripe), and with the findings of Teplov *et al.* [6] that there are *two different* copper sites in $TmBa_2Cu_3O_7$ in the planes, having a ratio of appearance of 2:1.

The $(Sr_xCa_{1-x})_2CuO_3$ class of materials, having only well-isolated chains with $\delta = 0$, has become popular now because of its highly anisotropic antiferromagnetic behavior. Figure 2 shows our LDA band structure of Sr_2CuO_3. Of course, it does not account for the correlation gap in the dp-σ^* band; however, its dispersion along and perpendicular to the chains yields the anisotropy of the hopping matrix element t and hence of the exchange coupling $J \sim 4t^2/U$. The anisotropy ratio of J in the plane containing the plaquettes is huge; practically only dipole–dipole coupling is expected in this transversal direction. For the plane perpendicular to the plaquettes but containing the chains, we estimate $J_\perp / J_\parallel \sim 3 \times 10^{-3}$ for Sr_2CuO_3 and $\sim 10^{-2}$ for Ca_2CuO_3.

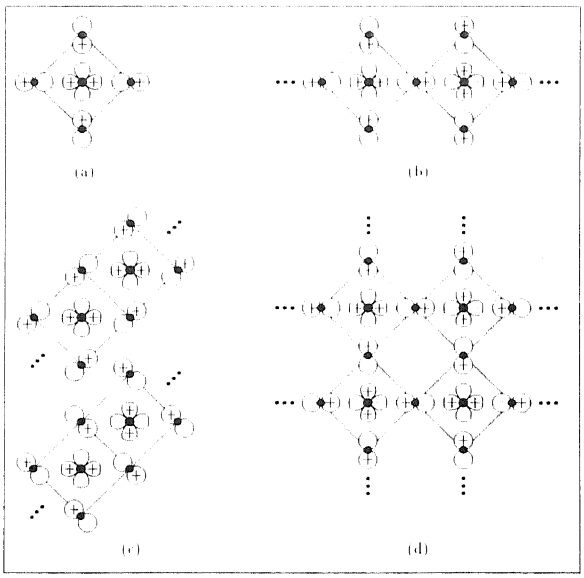

Fig. 1. Anionic cuprate structures, with the antibonding state depicted. For details see the text.

2. EXACT DIAGONALIZATION STUDIES FOR CHAIN CLUSTERS

The situation described above makes a theoretical understanding of doped CuO_3 chains crucial. To study the interplay of hole doping, electron–electron, and electron–lattice interactions, we adopted a four-band (pd) extended Peierls–Hubbard model, which, if necessary, is further reduced to two-band and one-band Peierls–Hubbard models and to Heisenberg models, respectively. Our standard set of parameters is $U_d = 10.5$ eV, $U_p = 4$ eV, $V_{pd} = 1.3$ eV, $t_{pd} = 1.3$ eV, $t_{pp} = 0.65$ eV, $\Delta\varepsilon_{pd} = 3.6$ eV.

First we consider the evolution of the site-resolved occupation numbers vs. δ within the exact diagonalization technique (ED, Lanczos). We compare the results with frequently used approximations: restricted Hartree–Fock (HF), Local Ansatz (LA) [7], no double occupancy of Cu sites ($U_d \to \infty$), or of both O and Cu sites (SLF, spinless fermions). The latter two are obtained within the ED by taking large values of U_d and U_p, respectively, $\gtrsim 100$ eV and a $1/U$ extrapolation for $U \to \infty$. The results are shown on Fig. 3 of Ref. 1. As expected, the mean-field like approximations (HF, LA) reveal large deviations near $\delta = 0$ but yield an accurate description near $\delta = 1$, just opposite to the approximations which forbid double occupancy. For the CuO_3 chains in the 123 structure and in the charged stripes of $(La, Sr)_2CuO_4$, when $\delta \approx 0.5$ is realized, all approximations yield comparable and sizable deviations from ED.

The calculated spin and charge structure factors exhibit maxima at $2k_F$ for $\delta = 0$ and -0.5 (electron doping) and at $4k_F$ for $\delta = 0.5$ (hole doping) [1]. The maxima at $2k_F$ in the spin structure factors are regarded as precursors of the spin density wave (SDW) or the Néel state, which is observed for $(Sr, Ca)_2CuO_3$, and is triggererd by weak interchain exchange. The experimentally observed chain-related $2k_F$ fluctuations [8] near $\delta = 0.5$ (dynamical charge density wave, CDW, or SDW) for $YBa_2Cu_3O_7$ and

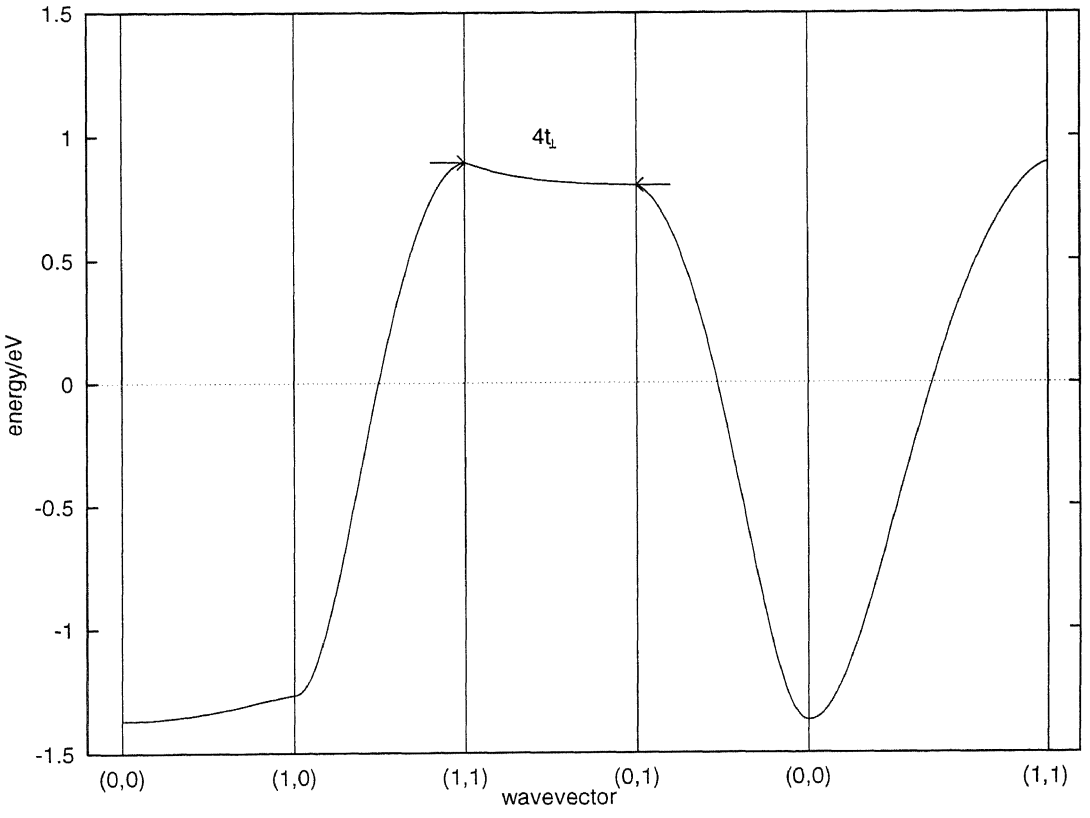

Fig. 2. LDA band structure for Sr_2CuO_3 around the Fermi level.

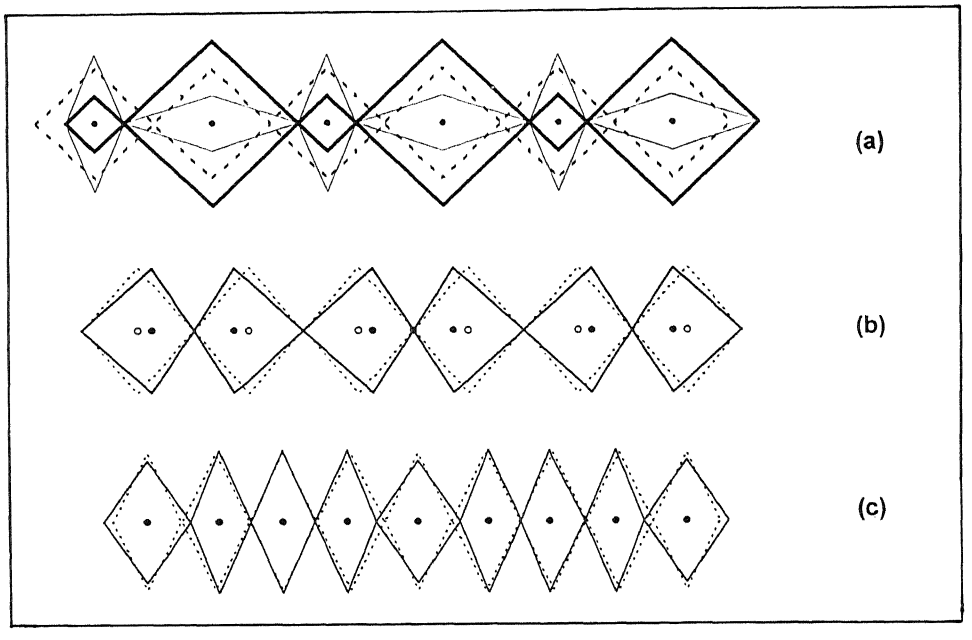

Fig. 3. Schematical view of lattice distortions (exaggerated). Undistorted chains are denoted by dotted lines and the corresponding Cu positions by open circles. (a) $2k_F$ Cu–CDW–O–BOW state for $\delta = 0$ in the weak correlation case, or alternatively, $4k_F$ state for $\delta = 0.5$ in the strong correlation case (thin and thick lines for two different crystal field situations). (b) Spin-Peierls state (strong correlation case, $\delta = 0$). (c) $2k_F$ Cu–CDW–O–BOW state for $\delta = 0.5$ in the weak correlation case expected for the CuO_3 chains in $RBa_2Cu_3O_7$ compounds and in charged stripes in the CuO_2 plane at $\langle\delta\rangle = 1/8$.

the static stripe superstructures in $La_{1.875}Sr_{0.125}CuO_4$ [3,9], corresponding to a period-4 (i.e., $2k_F$) superstructure along the charged stripe, should be interpreted as a strong hint for reduced correlation effects at these doping levels. (Compare also the discussion below of the superstructures affected by the electron–lattice interactions.)

In a next step we allow for different oxygen on-site energies ε_p for the nonequivalent apical and in-chain oxygens. Comparing the calculated occupation numbers with the observed XAS O 1*s* cross-sections for $YBa_2Cu_3O_7$ [10], we deduce a sizable difference $\Delta\varepsilon_{pp} = 2 \pm 0.5$ eV. As a result the energy distance of the apical oxygen state from the plane Cu state is quite large, 5–6 eV, which is of fundamental interest for the stability of the Zhang–Rice singlet [11].

Considering electron transfer integrals and nearest-neighbor Coulomb interaction V_{pd} to be bond-length dependent, we look for the minimum of the total energy of the four-band Hamiltonian and its projections mentioned above by treating the lattice degrees of freedom as classical variables in the harmonic approximation. Considering *odd numbered* periodic rings we found kink solutions for arbitrarily weak electron–lattice interaction. From the kink tails the character of the superstructure of a long periodic chain can be estimated [12]. For $\delta = 0$, we find either a spin-Peierls ground state (Cu site bond order wave, BOW, and a weak CDW on in-chain oxygen sites) for typical strong on-site Coulomb correlation, and in the opposite limit a CDW state involving Cu and the apical oxygen (BOW for in-chain oxygen). For $\delta = 0.5$ in the strong correlation parameter region a $4k_F$ mixed BOW–CDW solution has been found. The transition to the weaker coupled $2k_F$ mixed BOW-CDW as well as the absence of the spin-Peierls state in $Sr(Ca)_2CuO_3$ are quantitatively not yet understood. Typical calculated distortions of CuO_3 chains are schematically depicted in Fig. 3.

Financial support from the Deutsche Forschungsgemeinchaft and the Max-Planck-Gesellschaft is gratefully acknowledged (S.-L.D. and J.M.).

REFERENCES

1. S.-L. Drechsler *et al.*, *Phys. Rev. B* **55**, 606 (1997).
2. L. F. Mattheiss, *Phys. Rev. B* **49**, 14050 (1994).
3. A. Bianconi, *Solid State Commun.* **89**, 933 (1994).
4. J. M. Tranquada, *Ferroelectrics* **177**, 43 (1996).
5. M. A. Teplov *et al.*, Proc. NATO-ASI "*Material Aspects of High-T_c Superconductors: 10 Years after the Discovery*," August 1996, Delphi, Greece, (Kluwer, Dordrecht), in press.
6. V. J. Emery *et al.*, these proceedings and Preprint *Sissa. Cond. Mat* 9610094.
7. A. Oles and W. Grzelka, *Phys. Rev. B* **44**, 9531 (1991).
8. H. A. Mook *et al.*, *Phys. Rev. Lett.* **77**, 370 (1996), and these proceedings.
9. J. B. Goodenough, these proceedings.
10. N. Nücker *et al.*, *Phys. Rev. B* **51**, 8529 (1995).
11. R. Raimondi *et al.*, *Phys. Rev. B* **53**, 8774 (1996).
12. J. Malek *et al.*, submitted to *Phys. Rev. B* (1997).