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Effects beyond the pdσ-model in the low-energy physics of cuprates

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Abstract

The role of orbitals beyond the Cu 3d O 2pσ set employed in the widely used extended Hubbard model is considered with respect to low-energy charge excitations in cuprates. We focus on the description of the EELS and optical conductivity data of Sr_2CuO_3 and $Sr_2CuO_2Cl_2$ with respect to O 2pπ states. Consequences for the orbital character of doped holes are discussed. The achieved novel description of the EELS data in transverse chain response is robust with respect to the addition of Cu $3d_{xy}$ and 4s orbitals.

Keywords: Sr_2CuO_3; $Sr_2CuO_2Cl_2$; La_2CuO_4; $CaCuO_2$; EELS; O 2pπ orbitals; Extended Hubbard model

The reliable knowledge of the orbitals involved in low-lying charge excitations of cuprate insulators and in quasi-particles in the ground state of hole doped cuprates is crucial for the determination of an appropriate microscopic Hamiltonian which should describe universally these strongly correlated compounds in a realistic fashion. So far, the pdσ-extended Hubbard model is considered as the main candidate for that purpose. However, in a combined theoretical and experimental study devoted to Sr_2CuO_3, we have shown its failure in describing properly its low-energy loss function (LF) $\mathrm{Im}\text{-}1/\varepsilon(\omega,\vec{q})$ measured in electron energy loss spectroscopy (EELS) in transverse response, i.e. for $\vec{q}\perp$ to the chain axis [1]. This problem can be resolved, if also the O 2pπ orbitals within the x,y-plane of the CuO_4 plaquettes are included into the basis set beside the standard $3d_{x^2-y^2}$ and O 2pσ states. However, one may ask, is this choice unique? Here we show, that the achieved picture is robust with respect to the account of other candidates such as Cu $3d_{xy}$ and Cu 4s (Fig. 1) [2]. Moreover, even the specific asymmetric shape of the low-energy peak is now well reproduced. The slight upward shift by about 0.3–0.5 eV compared

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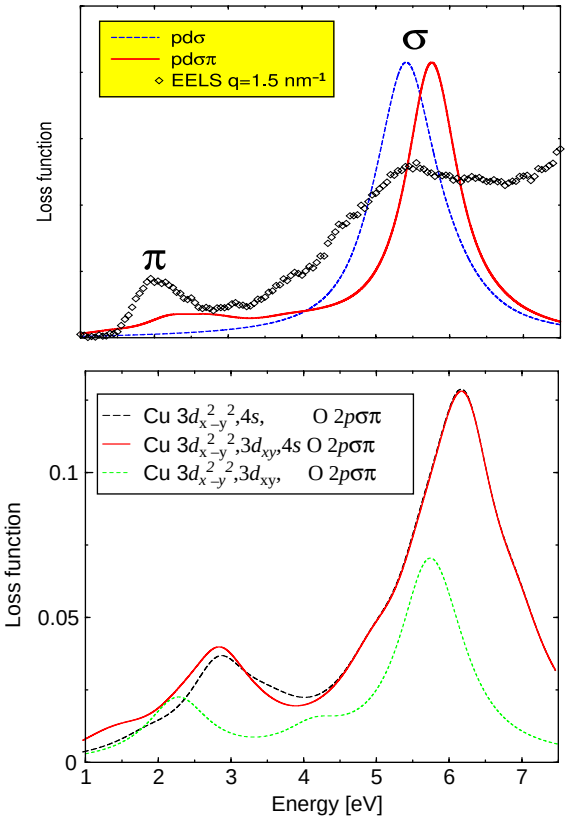

Fig. 1. Loss functions for chain-like corner-shared CuO clusters in transverse response for various orbital sets employed. Comparison with raw EELS data (unnormalized loss probability) for Sr_2CuO_3 and simple pdσ (σπ)-models (upper panel). Note the missing peak near 2 eV in the standard pdσ-model.

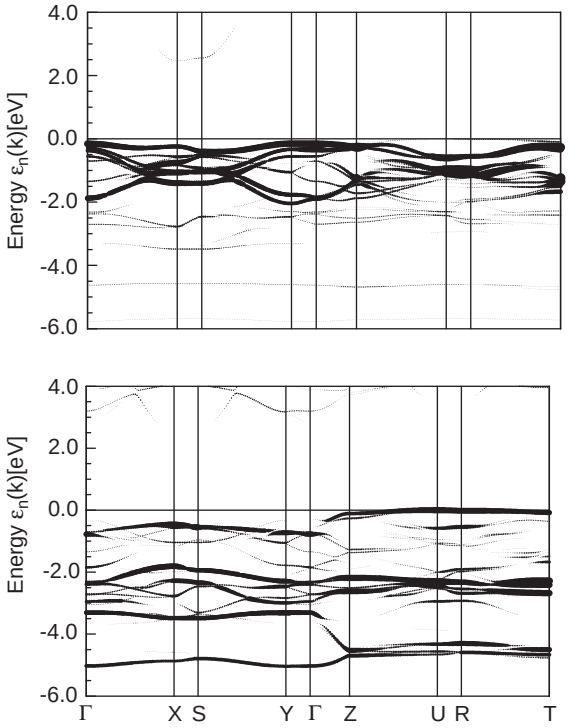

Fig. 2. O 2p orbital character of the bands near E_F measured by the thickness of the lines within LDA + U for Sr_2CuO_3 . The chains are running along the x-axis. Notice the dominant π contribution (upper panel) for the uppermost valence states below the charge transfer gap compared with the σ contribution (lower panel). These states determine the character of the first doped holes to first approximation.

with the low-energy peak in the experimental LF can be ascribed to the remaining finite size effect caused by the small cluster size allowed for the exact diagonalization studies employed. Here we adopt the following main parameters for the part added to our original pdσπ extended Hubbard-type Hamiltonian: $\varepsilon_{d_{xy}} = 2.5, \varepsilon_s = -1.8, U_{d_{xy}} = U_{d_{x^2-y^2}} = 9, U_s = 3.5, U_{dd} = 8.2, U_p = 6, t_{dp\pi} = 0.7, t_{pd\sigma} = 1.4, t_{sp} = 1.75$ (all energies in eV; for the other parameters see Ref. [1]). Due to the sizeable U_s, the Cu 4s orbitals are occupied with about 0.5 electrons in accord with the Cu-NMR analysis of La_2CuO_4 [2].

Most of the parameters found are in accord with full-potential LDA + U band structure calculations devoted to Sr_2CuO_3 (see Fig. 2), $CaCuO_2$, and $Sr_2CuO_2Cl_2$ [3]. In particular, within the hole picture the on-site energies of O 2pσ states are shifted up by about 1 eV compared with the predictions of standard LDA calculations. This is a consequence of the reduced covalency splitting caused by the large onsite Coulomb repulsion $U \sim 8$ eV at the Cu sites. Therefore, at fixed Hamiltonian parameters the doped holes which form essentially the quasi-particles, aquire a non-negligible O 2pπ weight. We found that the doped holes occupy the O 2pσ orbitals only to 50% . To 45% they reside on O 2pπ states and to 5% on Cu 3d$_{x^2-y^2}$ states. As a consequence, the binding energy of the Zhang–Rice singlet is reduced and the widely used approximation of total

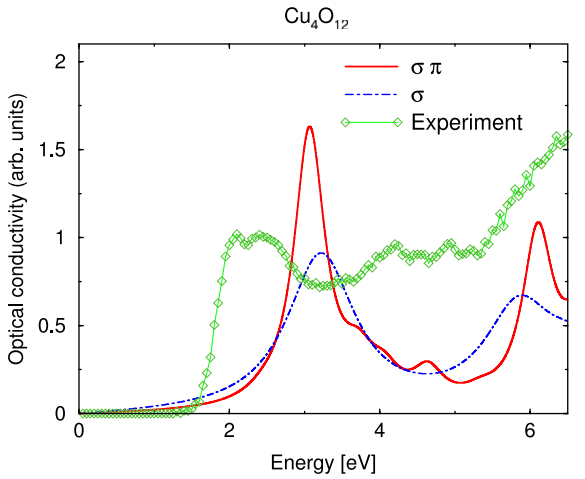

Fig. 3. Optical conductivity $\sigma(\omega, q)$ derived from EELS data in $Sr_2CuO_2Cl_2$ for transferred momentum $q = 1\,\mathrm{nm}^{-1}$ within the CuO_2 plane (**q** along [1 1 0]) in comparison with theoretical $\sigma(\omega, 0)$ curves for a periodic 2×2 Cu_4O_8 cluster within the usual pdσ-model (σ) and inplane O 2pπ states included (σπ).

suppression of double occupancy of the Cu $3d_{x^2-y^2}$ orbital is better obeyed even at large hole doping [4].

To exclude an occasional failure of the pdσ-model in Sr_2CuO_3 only, we have to discuss also other cuprates. With this aim, we consider now the layered system $Sr_2CuO_2Cl_2$ (Fig. 3). The experimental three-peak structure (main peaks near 2, 4.5, and 6 eV) is qualitatively reproduced. From the comparison with Fig. 1, we suggest that the missing weight around 4.5 eV should be ascribed to transitions involving Cu 4s states. The double peak structure near 2 eV in Fig. 3 compares to the peak-shoulder feature near 3 eV again upwards shifted by finite size effects. Remarkably, the lowest charge excitation has mixed O 2pσπ character like for Sr_2CuO_3. Then it becomes clear why the low-energy peak of the double peak structure near 2 eV shows only weak dispersion with increasing q in the EELS spectra. Also in the 2D case the doped holes aquire mixed character (at least at very low hole doping).

To conclude, a general essential incompleteness of the standard pdσ-model for all cuprates in the sense discussed above is very likely, although its success in describing particular features is well known.

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