The electronic structure of $Ba_2Cu_3O_4Cl_2$

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Abstract

Band structure calculations for $Ba_2Cu_3O_4Cl_2$ within the local density approximation (LDA) have been carried out and the total as well as partial densities of states have been calculated. The investigated compound is similar to the antiferromagnetic parent compounds of cuprate superconductors but contains additional Cu(B) atoms in the planes. Within the LDA metallic behaviour is found with two bands crossing the Fermi level. The result is in disagreement with the experimentally observed antiferromagnetic insulating state, showing the necessity to deal with the electron correlations in a more detailed way. To decide which orbitals should be correlated, a model with Cu-3d and O-2p orbitals was constructed. It is shown that the coupling between the Cu(A) and the additional Cu(B) subsystem is small.

Keywords: $Ba_2Cu_3O_4Cl_2$; Band-structure calculation; Tight-binding model

Layered copper oxides with CuO_2-planes have been investigated extensively in recent years. In the undoped case, these materials are antiferromagnetic charge transfer insulators. Photoemission measurements of the hole dispersion in $Sr_2CuO_2Cl_2$ [1] showed rough agreement with the dispersion expected from an extended t–J model. Recently, a similar dispersion was also measured in $Ba_2Cu_3O_4Cl_2$ [2] despite the existence of additional Cu(B) atoms in the plane. Moreover, this compound shows unusual magnetic properties like two copper spin subsystems with Néel temperatures different by one order of magnitude [3]. Therefore, we will clarify here the influence of the additional Cu(B) atoms on the electronic structure of $Ba_2Cu_3O_4Cl_2$.

One typical strategy to take into account the strong correlations in copper oxides is characterized as follows: the relevant orbitals which determine the electronic structure near the Fermi level are found from a band structure calculation. Using these orbitals a

multi-band Hubbard model is constructed. In most cases it can be projected to an effective one-band t–J-like model. Here we want to present the first steps on this way: the band structure calculation, the determination of the relevant orbitals and a first discussion how the known ideas for the CuO_2-plane should be modified.

We carried out a LDA band structure calculation using the linear combination of atomic orbitals (LCAO). For the exchange and correlation potential the parametrisation of von Barth and Hedin was chosen. We used a scalar relativistic scheme with a minimum basis. We have chosen the valence states Cu(4s,4p,3d), O(2s,2p), Ba(6s,6p,5d) and Cl(3s,3p), and the lower-lying states treated as core states. $Ba_2Cu_3O_4Cl_2$ occurs in bct-structure with $a = 5.51$ Å and $c = 13.822$ Å [4]. It has a relatively open structure. Therefore, we introduced four empty spheres. The main part of the potential, the Hartree contribution, is constructed as a sum of overlapping spherical contributions. The exchange and correlation potential is calculated in atomic sphere approximation.

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The calculation results in a paramagnetic and metallic behaviour with two bands crossing the Fermi level (see Fig. 1). These two bands have no dispersion in z-direction. That means that the corresponding bonds lie in the x–y-plane. From the partial DOS it can be seen which states contribute to these bands (see Fig. 2). The broad band is essentially formed by a Cu(A)d–Op-hybridization, whereas the narrow band is built by Cu(B)d–Op-hybridization. Ba and Cl do not contribute to the states in the corresponding energy region.

Partial net occupations have been calculated m-resolved. Holes exist only in the $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals of the five Cu-3d-orbitals. The net occupation of Cu(A) and Cu(B) are 0.52 and 0.75 holes for the $3d_{x^2-y^2}$ orbital and 0.34 and 0.11, respectively, for the $3d_{3z^2-r^2}$ orbital. The hole occupation of the O-2p$_z$ orbital (0.2) is essentially smaller than the occupation of the O-2p$_{x(y)}$ orbitals (0.7).

This indicates the dominance of pdσ-bonds. The essential part of holes in the copper-d-orbitals belongs to the $3d_{x^2-y^2}$ orbitals. The higher occupation of the $3d_{3z^2-r^2}$ orbital of Cu(A) compared to Cu(B) is due to the Cl atom, which lies above the Cu(A) site in the unit cell. More detailed investigations show that the $3d_{3z^2-r^2}$ states are further apart from the Fermi level than the $3d_{x^2-y^2}$ states. This justifies for a first analysis the restriction to the pdσ bond between Cu-3d$_{x^2-y^2}$ and O-2p$_{x(y)}$.

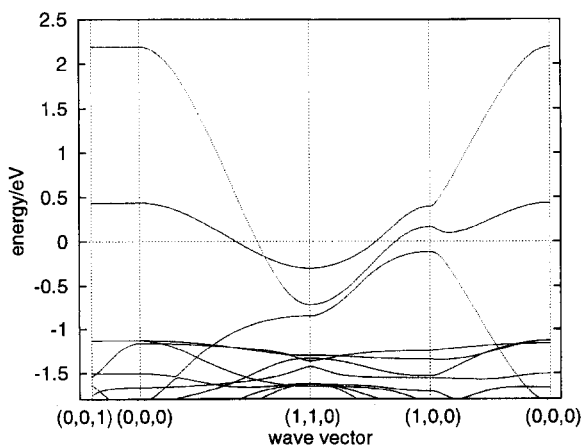On the basis of these ideas we construct a tight-binding model with the above-mentioned orbitals

Fig. 2. Total and partial DOS of Ba$_2$Cu$_3$O$_4$Cl$_2$, the Fermi level is at zero energy.

Fig. 1. LCAO–LDA band structure of Ba$_2$Cu$_3$O$_4$Cl$_2$, the Fermi level is at zero energy. The wave vector is measured in units of ($\pi/a, \pi/a, \pi/c$).
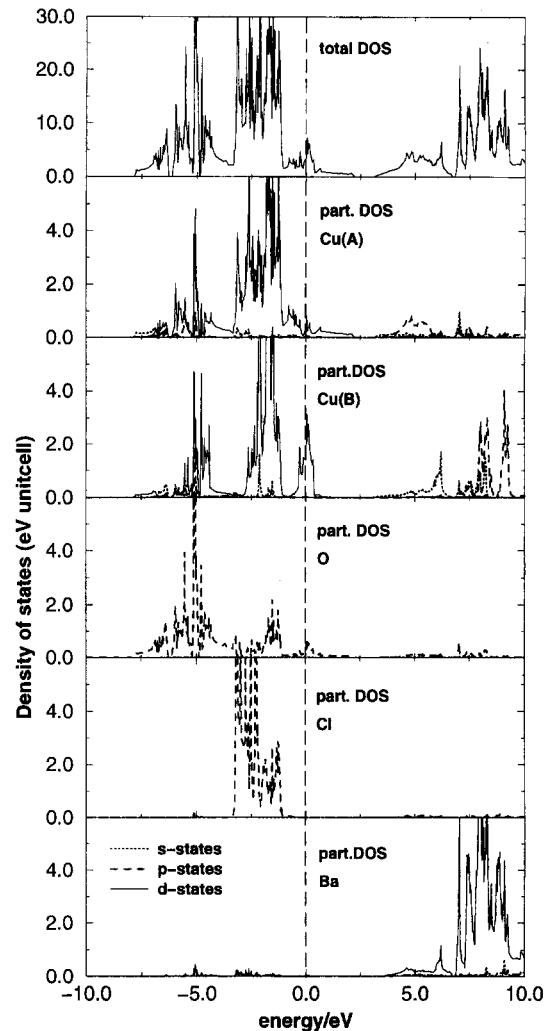
(Fig. 3). There are one Cu(B) site, two Cu(A) sites and four O sites in the unit cell. The overlaps t_{pd} between Cu-3d$_{x^2-y^2}$ and O-2p$_{x(y)}$ and the overlaps $t_{pp}^{\perp}$ and $t_{pp}^{\parallel}$ between two different O sites are taken into account. The sign convention of the model follows from the signs of the orbitals whose phase factors are chosen as in Fig. 3. The on-site energies of Cu(A) and Cu(B) are considered to be different.

The dispersion of the Cu(A) band is determined by t_{pd} and $t_{pp}^{\perp}$, the dispersion of the Cu(B) band only by $t_{pp}^{\perp}$. The coupling of the two systems takes place only
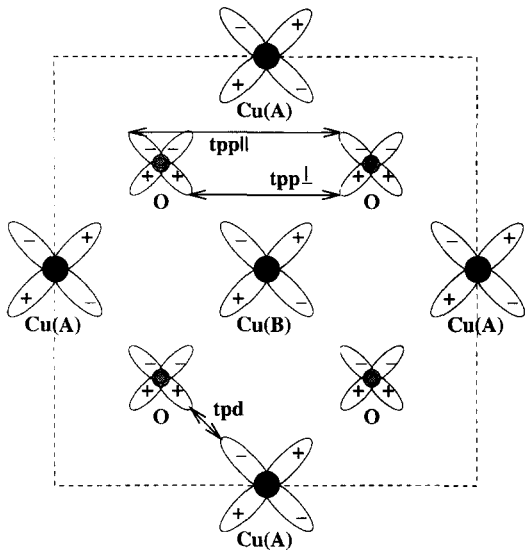
Fig. 3. Tight-binding model of the Cu_3O_4–plane in $Ba_2Cu_3O_4Cl_2$. The relevant Cu-$3d_{x^2-y^2}$ and O-$2p_{x(y)}$ orbitals with the chosen phase convention as well as the considered overlap integrals t_{pd}, $t_{pp}^\perp$ and $t_{pp}^\parallel$ are plotted.

Fig. 4. Band structure of the tight-binding model for the set of parameters which is mentioned in the text. The energy-scale is chosen such that $\varepsilon_O = 0$ and the wave vector is measured in units of $(\pi/a, \pi/a)$.

through $t_{pp}^\parallel$ which leads to a hybridization of the bands between the points $(1,1)$ and $(1,0)$ (Fig. 4). The size of the parameters can be roughly estimated already from the LDA band structure (Fig. 1). The larger bandwidth of the $Cu(A)$ band with respect to the $Cu(B)$ band leads to $t_{pd} > t_{pp}^\perp$ and the small hybridization between these bands can only be explained if $t_{pp}^\parallel$ is the smallest parameter.

We obtain a rather good agreement of the so defined tight-binding model with the band structure calculation (cf. Figs. 1 and 4) if we choose the following parameters: $\varepsilon_{Cu(A)} = 0.25$ eV, $\varepsilon_{Cu(B)} = 0.75$ eV, $\varepsilon_O = 0$, $t_{pd} = 1.7$ eV, $t_{pp}^\perp = 0.45$ eV, $t_{pp}^\parallel = 0.20$ eV. We expect that the remaining deviations can be reduced by the use of additional overlap integrals. Except from the on-site energies these parameters are in rough agreement with the parameters known from the usual CuO_2-plane [5]. It is clear that a simple tight-binding fit of a LDA band structure yields too small values for the charge transfer energy $\Delta = \varepsilon_{Cu(A)} - \varepsilon_O$ which cannot explain the charge transfer gap of about 2 eV. In order to determine these values, as well as the on-site correlation energies, total energy calculations are necessary, which were not carried out here. Since the charge
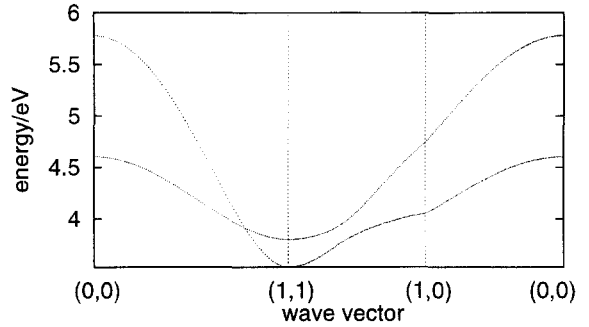
transfer gap is of similar size as in usual cuprates it seems reasonable to use here the same on-site and correlation energies. However, the modification due to the additional $Cu(B)$ has to be taken into account. We find a difference in the on-site energies at the Cu sites of 0.5 eV. This agrees with the difference of the on-site energies from the Slater–Koster integrals of the LCAO calculation. We expect that this energy difference remains unchanged in a more sophisticated determination of on-site-energies.

From these considerations it can be concluded that there are two relatively isolated subsystems in the cuprate plane of $Ba_2Cu_3O_4Cl_2$ which interact only through the small parameter $t_{pp}^\parallel$. So it can be understood that the additional Cu has no drastic influence on the one-hole dispersion [2]. A simple perturbation theory yields the following estimations for the exchange integrals: $J_{AA} \propto t_{pd}^4/\Delta^3$, $J_{BB} \propto t_{pd}^4(t_{pp}^\perp)^2/\Delta^5$, $J_{AB} \propto t_{dp}^4(t_{pp}^\parallel)^2/\Delta^5$.

These estimations explain in principle that the Néel temperatures of the two copper spin subsystems of this compound differ by one order of magnitude.

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