COMMENT

Comment on 'The electronic structure of CaCuO$_2$ and SrCuO$_2$'

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Abstract. Recent electronic structure calculations for the title compounds performed by Wu *et al* [1] are critically reconsidered, applying high precision full-potential bandstructure methods. It is shown that the bandstructure calculations presented by the authors contain several important inconsistencies, which make their main conclusions highly questionable.

In a recent paper Wu *et al* [1] presented bandstructure calculations for the quasi one-dimensional CuO-chain compound SrCuO$_2$ and the quasi two-dimensional material CaCuO$_2$, both being of prototypical character and therefore of general interest. Wu *et al* used a full-potential linear combination of atomic orbitals method [2] in the framework of the local spin density approximation (LSDA) and included on-site Coulomb interaction corrections (LSDA+U). The authors of [1] claim that on the basis of their full-potential band structure experimental findings can be well fit with an U of 5 eV, significantly smaller than U values reported in previous calculations [3].

However, there are obvious inconsistencies and important differences between the calculations of [1] and previous studies [3–6], concerning (i) the proper symmetry in k-space, (ii) the widths and the orbital character of the shown bands, (iii) the total densities of states (DOS) as well as the partial densities of states (PDOS). Therefore, we reinvestigated the electronic structures of CaCuO$_2$ and SrCuO$_2$ using two independent, well basis converged full-potential bandstructure methods to find out whether or not the differences mentioned above could be understood as a consequence of the differences between a full-potential [1] and the earlier non-full-potential calculations [3,5,6]. We carried out LSDA bandstructure calculations for CaCuO$_2$ within a full-potential minimum-basis local-orbital scheme (FPLO) [7] and within a full-potential linearized augmented plane wave (FLAPW) scheme [8], both in scalar relativistic versions. (We note that relativistic effects are of the order of 0.1 eV only.) In the FPLO-scheme, modified Ca 3d, 4s, 4p, (Sr 5s, 5p, 4d), Cu 3d, 4s, 4p and O 2s, 2p, 3d states were used as valence states for CaCuO$_2$ (SrCuO$_2$), the lower lying states were treated as core states. The WIEN97-code [8] employs local orbitals (LO) to relax linearization errors and to treat the O-2s and semicore Cu-3p and Ca-3s, 3p states. Well converged basis sets of over 500 APW functions plus LOs were used. The radii of the atomic spheres in the latter case were 1.8 a.u. for all atoms. The basic calculations were performed with 125 and 90 k-points in the FPLO-scheme and in the WIEN97-code, respectively, for the irreducible part of the Brillouin zone using the tetrahedron method. We emphasize that the numerical convergence

(with respect to the number of k-points N_k, the valence basis set, the potential and the density representataion) of all calculated properties was carefully checked. Following [1], we will discuss first $CaCuO_2$ and afterwards $SrCuO_2$.

CaCuO$_2$

First, we will concentrate on the bandstructure and then on the DOS. Both bandstructures obtained with the FPLO and WIEN97 codes agree excellently with each other (see figure 1(a)) and with previously published results [4, 5]. Considering the bands in [1] one realizes the following points: The authors show a bandstructure with *orthorhombic* symmetry for the *tetragonal* crystal structure [9] (note the different dispersions in figure 1(a) of [1] along the Γ-(100) and Γ-(010) direction, respectively, which must be equivalent for the tetragonal case). Also, the band degeneracies at symmetry points are incorrect. As a consequence, the number of degeneracies in Γ-(001) direction (c-direction) differs from all other calculations (11 different bands instead of 8 different bands allowed by the crystal symmetry). Contrary to our results and to the results of Refs. [4, 5], the authors find an additional, third band with sizable dispersion with its maximum at (001). We analysed the orbital character of our bands, in particular to find out which states are responsible for the relatively large dispersion in the c-direction of about 1–2 eV discussed also by Mattheiss *et al* [5]. Our calculations show that these two strongly dispersive bands have predominant O $2p_z$ character with a small admixture of Cu $3d_{3z^2-r^2}$ states. In contrast, the c-dispersion of the antibonding band essentially made up by O 2p-σ and O 2p-π orbitals with the Cu $3d_{x^2-y^2}$ orbital is only about 350 meV. Just these states mediate the magnetic coupling between different layers. This confirms the quasi-two-dimensional character of the magnetic Hamiltonian.
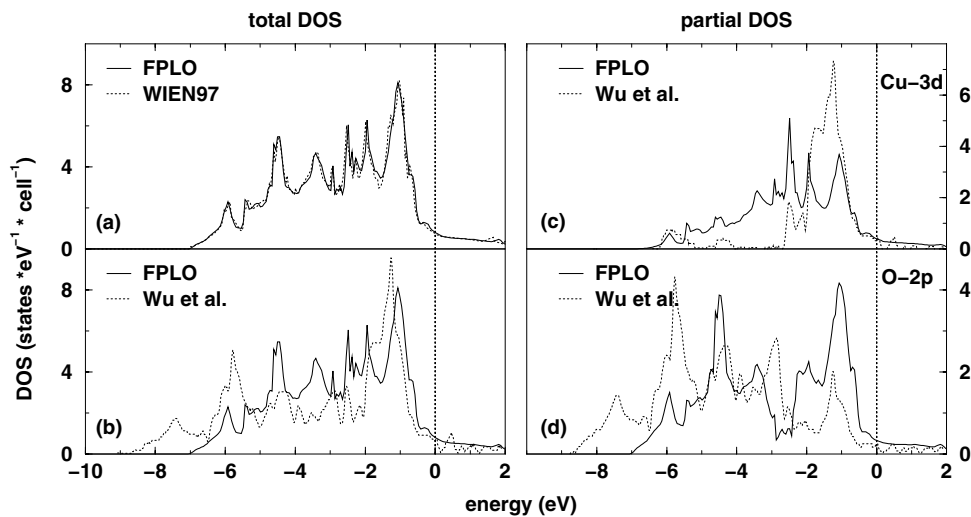

Figure 1. Total DOS (a,b) and partial DOS (c,d) of CaCuO$_2$ calculated within various bandstructure schemes (see text).

In figure 1(b) we compare our results for the DOS with those of figure 2(a) in [1]. The width of their pd-complex is too large by about 2 eV. The authors attribute this discrepancy to their choice of an ionic basis, which only means that their calculations are not basis set converged. The reason for the large discrepancy between the DOS of [1] and our's is evident from figures 1(c) and 1(d). Due to the ionic orbital basis used in [1], the O 2p states are shifted

downwards by about 2 eV and the hybridization with Cu 3d states is consequently reduced. We attribute simply the reduction of the bandwidth in the LSDA+U in the calculation of [1] to a downwards shift of their Cu 3d states towards the incorrectly positioned oxygen 2p states.

SrCuO$_2$

For our paramagnetic calculation the resulting DOS is in excellent agreement with the DOS reported in [6, 11]. One should note that the occurrence of van-Hove singularities at the band edges of the antibonding band, due to the nearly one-dimensional electronic structure of the compound, depends critically on the sufficiently large N_k used in the calculation.
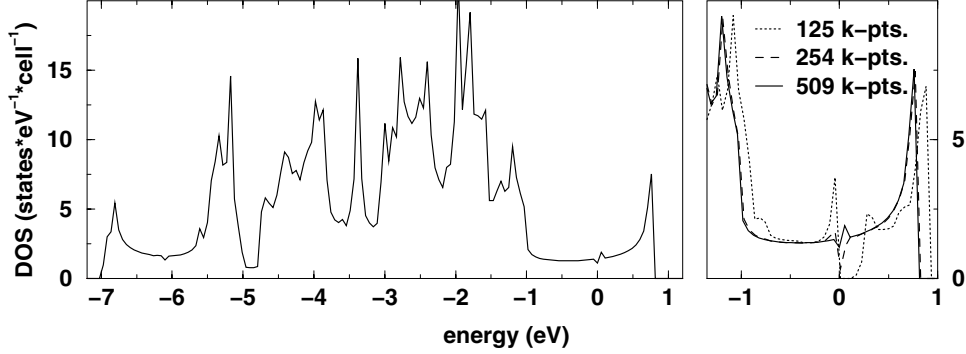

Figure 2. FPLO total DOS for SrCuO$_2$ of the pd-complex (left panel) and the zoomed region near the Fermi level for different number of k-points (right panel), calculated in the doubled unit cell.

For the supercell calculation, we doubled the unit cell along the chain direction and started the self-consistent calculation with an antiferromagnetic arrangement of the Cu spins along the chains [12]. To describe properly some peculiarities related to the nearly one-dimensional electronic structure, we made several calculations varying N_k. In particular, we enlarged N_k along the chain direction. The results are shown in figure 2. Due to the nearly ideal one-dimensional dispersion of SrCuO$_2$, the calculation results in an erroneous insulating groundstate for an *insufficient* N_k. At least for $N_k > 250$, the artificial gap and the related singularities disappear and the results converge towards those of our paramagnetic calculation. Possibly, the gap of 0.55 eV in [1] can be attributed qualitatively to an insufficient number of k-points. The reported relatively big magnetic moment of $0.33\mu_B$ is related to this artificial gap and to the unusualy small hybridization of the Cu 3d states with the O 2p states. An antiferromagnetic solution has been reported also by other authors [6] though with an even smaller gap and extremely small magnetic moments for the SrCuO$_2$-system. Again, we attribute this gap (notably smaller than that in [1] due to a larger N_k) to a still too small number of k-points. To make this point more clear let us consider schematically the band structure in the folded zone picture in Γ-(001) direction near the antiferromagnetic Bragg point (see figure 3). The weak hybridization between the two subchains of the double chain leads to two slightly split bands. After the folding of these two bands in the doubled unit cell, new crossing points appear close to the new symmetry plane. Therefore, DOS routines result in a wrong interpolation if the crossing points are not at calculated k-points. The splitting $\Delta_{max} \approx$ 150 meV mentioned above (see figure 3) provides an upper bound for the artificial gap [13]. Hence, for supercell calculations, especially for quasi-one-dimensional electronic structures, one has to be very careful choosing N_k in applying standard interpolation methods.

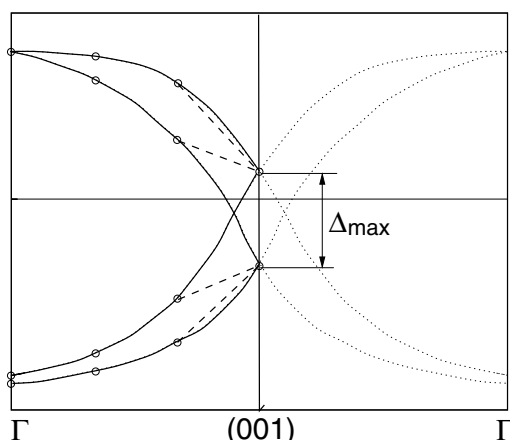In figure 4(a) of [1] one finds the Cu 3d states in the PDOS with a too small width as

Figure 3. Schematic picture of the folded antibonding bands in Γ-(001) direction in SrCuO$_2$. The solid lines are the correct bands, the dashed lines show the interpolated bands for the k points given by the open circles. For explanation see text.

already discussed for CaCuO$_2$. Moreover, for an orbital projected DOS, it is reasonable to use symmetry related orbitals with their quantization axis perpendicular to the CuO$_4$ plaquette. In this representation only the Cu 3d$_{x^2-y^2}$ orbital contributes considerably to the antibonding band (instead of two Cu 3d orbitals shown in figure 4 of [1]), as found for CaCuO$_2$ (figure 1(a) of [1]). The LSDA+U procedure used in [1] depends on the basis set representation and would require therefore the application of the same local orbital symmetry for both compounds in order to ensure a proper comparison between them.

To summarize, we discussed the main differences between the results of Wu *et al* and our, or previously published data [3–6, 11], basic paramagnetic LDA calculations contain several serious inconsistencies, all conclusions reported in [1] with respect to LSDA+U are highly questionable. In particular, the large gap in SrCuO$_2$ at moderate U might result from the artificial gap found in their LSDA calculations.

Acknowledgments

References

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[12] We suppose that the authors calculated the same magnetic unit cell and spin structure, but there is no information about that in [1].
[13] A similar value of $\Delta_{max} \approx 150$ meV can be derived from figure 3 of [11]. The large gap of 550 meV reported in [1] clearly contradicts the claim of Wu *et al* to reproduce the bandstructure of [11] by backfolding.