

Comment on: "Energy band structures of the low-dimensional antiferromagnets Sr_2CuO_3 and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ " [J. Appl. Phys. 87, 4897 (2001)]

H. Rosner^{a)} and D. M. Johannes

Department of Physics, University of California, Davis, California 95616

S.-L. Drechsler

Institut für Festkörper- und Werkstofforschung Dresden, P.O. Box 270016, D-01171 Dresden, Germany

(Received 20 November 2000; accepted for publication 7 August 2001)

Recent electronic structure calculations for the title compounds performed by Wu *et al.* [H. Wu *et al.*, J. Appl. Phys. **87**, 4897 (2000)] are critically reconsidered by applying highly accurate full-potential band structure methods. It is shown that due to a nonconverged basis set the band structure calculations presented here by the authors disagree considerably with those of Wu *et al.*

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Recently, Wu *et al.*¹ presented band structure calculations for the one-dimensional antiferromagnetic chain compound Sr_2CuO_3 and the quasi two-dimensional material $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, both being of prototypical character and therefore of general interest. Wu *et al.* used a full-potential linear combination of atomic orbitals method² within the framework of the local (spin) density approximation (L(S)DA) and included on-site Coulomb interaction corrections (LSDA + U) at the Cu site.

However, there are considerable differences from previous full-potential linear muffin-tin orbital (FLMTO) calculations³ for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. Therefore, we reinvestigated the electronic structures of Sr_2CuO_3 and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ using two independent, full-potential band structure methods both with a well converged basis. We carried out LSDA band structure calculations for both title compounds within a full-potential minimum-basis local-orbital (FPLO) scheme⁴ and within a full-potential linearized augmented plane wave (FLAPW) scheme,⁵ both in scalar relativistic versions. In the FPLO scheme, modified Sr ($4s, 4p, 5s, 5p, 4d$), Cu ($3d, 4s, 4p$), O ($2s, 2p, 3d$), and Cl ($3s, 3p, 3d$) states were used as valence states, the lower lying states were treated as core states. The inclusion of Sr ($4s, 4p$) states was necessary to account for non-negligible core-core overlaps. The O and Cl $3d$ states were taken into account to further improve the completeness of the basis set. The WIEN97 code⁵ employs local orbitals (LOs) to relax linearization errors and to treat the O $2s$ and semicore Cu $3p$ and Sr ($4s, 4p$) states. Well converged basis sets of over 800 APW functions plus LOs were used. The radii of the atomic spheres in the latter case were 2.0 a.u. for Cu, Cl, and Sr and 1.6 a.u. for O, respectively. Self-consistent calculations were performed with 349 (428) and 405 (428) k points for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (Sr_2CuO_3) 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 representation) of all properties calculated was carefully checked.

Comparing our results with those presented in Ref. 1, we will discuss first $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. The density of states (DOS) for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ obtained within the FPLO scheme and WIEN97 code agree excellently with each other [see Fig. 1(a)] as well as with other previously published full-potential results³ [cf. Figs. 1(a) and 1(c)–1(e) and Fig. 3 of Ref. 3]. In Figs. 1(b)–1(e) we compare our results for the DOS with those of Fig. 2 in Ref. 1. The width of the pd complex published by Wu *et al.* is too large by about 1.5 eV. The reason for the large discrepancy between the DOS of Ref. 1 and ours is evident from Figs. 1(c)–1(e). Due to the nonconverged ionic orbital basis used in Ref. 1, the O $2p$ states and the Cl $3p$ states are shifted downward by about 1.5 and 3 eV, respectively, and the hybridization with Cu $3d$ states is consequently reduced. This results in the large peak at about -1 eV in the partial Cu $3d$ DOS in Fig. 1(b).

Wu *et al.* attribute this discrepancy to their choice of a special basis. They state⁶ that their chosen ionic basis reflects the strong ionic behavior of planar cuprates well while calculations using a neutral basis set (like FPLO or WIEN97) would overestimate the covalence. However, for any converged complete enough basis set, the calculational results of any band structure scheme using the well defined LDA should be *independent* of the basis. Of course, the choice of a biased nonconverged basis set can produce any electronic structure, in particular a structure which is also close to that of the experiment. However, such "agreement" has no meaning since by no choice of a basis set the well-known shortcomings of LDA can be improved. Poorly describing the strong Coulomb repulsion in cuprates, the LDA results generally in too small a difference between the on-site energies of Cu and O (Cl) states. The ionic basis set of Ref. 1 shifts the O and Cl states downward in an uncontrolled way. The better agreement with experimental data can therefore be considered as cancellation of errors by chance. Thus the relatively small values of U used in Refs. 1 and 7 should be attributed to the downward shift of the O $2p$ on-site energies.

^{a)}Electronic mail: helge@physics.ucdavis.edu

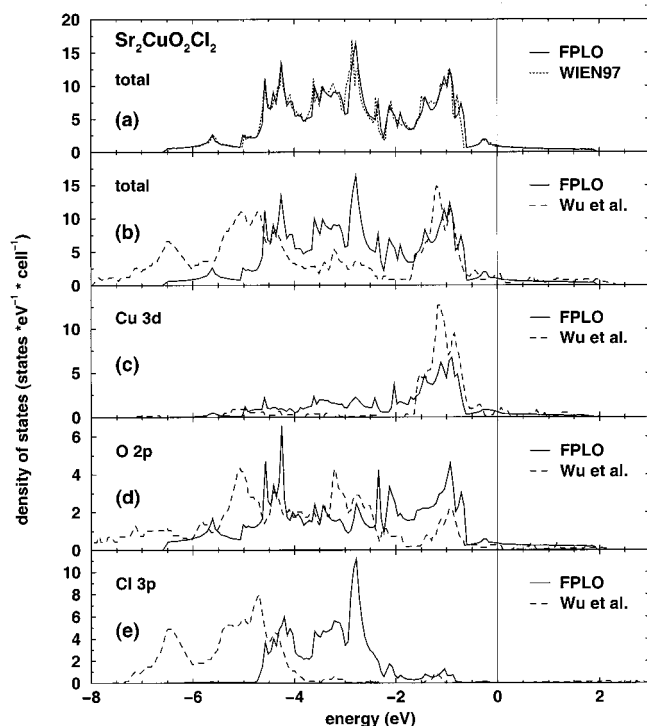


FIG. 1. Total DOS (a), (b) and partial DOS (c)–(e) of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ calculated within various band structure schemes.

By applying $L(S)DA+U$, the gap opens between the O $2p$ states and the unoccupied Cu $3d$ states, the downshifted O-derived states naturally require a smaller U to reproduce the empirical gap value.

Without repeating essentially all the issues mentioned above, we shall discuss Sr_2CuO_3 only briefly. As with the planar cuprate $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, the calculated DOS for Sr_2CuO_3 is in excellent agreement for both our calculations using different band structure schemes [see Fig. 2(a)]. The discrepancy between our calculations and those of Wu *et al.*¹ is evident from Fig. 2(b). It has the same origin as that mentioned for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. This is concluded from the position of the O $2p$ states in the partial density of states (not shown). In contrast to Ref. 1, we find a metallic solution within the LSDA calculations. The result of the LSDA for the doubled unit cell with initial antiferromagnetic polarization along the chains converges into the paramagnetic LDA solution. The antiferromagnetic and insulating solution presented in Ref. 1 should be ascribed most probably to underestimation of the pd hybridization. In fact, this artificial small hybridization

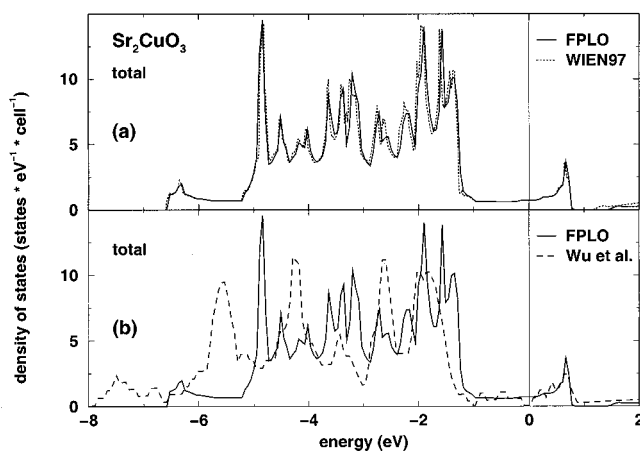


FIG. 2. Total DOS of Sr_2CuO_3 calculated within various band structure schemes.

due to the ionic basis set results in more localized moments at the Cu site which lead to overestimated spin splitting and finally to the insulating magnetic solution. In addition, the small number of k points in their calculation, obvious from the spiky DOS for the antibonding band, may influence the result as well.

To summarize, we have discussed the considerable differences between the results of Wu *et al.*¹ and our own findings as well as those of previously published data.³ The discrepancies appear most probably due to the use of a nonconverged ionic basis set in Ref. 1. The use of a nonconverged basis set might seem to give better agreement with experiment, but only by artificial cancellation of errors.

The authors acknowledge fruitful discussions with A. B. Shick and W. E. Pickett. They gratefully acknowledge the DAAD [a grant to one of the authors (H.R.)], the DFG [a grant to a second author (S.D.)], and the NSF (Grant No. DMR-9802076) for financial support.

¹H. Wu, Q. Q. Zheng, and H. Q. Lin, J. Appl. Phys. **87**, 4897 (2000).

²H. Wu, M. C. Qian, and Q. Zheng, J. Phys.: Condens. Matter **11**, 209 (1999).

³D. L. Novikov, A. J. Freeman, and J. D. Jorgensen, Phys. Rev. B **51**, 6675 (1995).

⁴K. Koepf and H. Eschrig, Phys. Rev. B **59**, 1743 (1999).

⁵B. Blaha, K. Schwarz, and J. Luitz, Comput. Phys. Commun. **59**, 399 (1990).

⁶H. Wu and Q. Q. Zheng, J. Phys.: Condens. Matter **12**, 5813 (2000).

⁷H. Wu, Q. Q. Zheng, X. G. Gong, and H. Q. Lin, J. Phys.: Condens. Matter **11**, 4637 (1999).