

## Self-interaction-corrected electronic structure of $\text{La}_2\text{CuO}_4$

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(Received 16 October 1992)

We have applied the self-interaction-corrected (SIC) local-spin-density-approximation (LSDA) formalism to  $\text{La}_2\text{CuO}_4$ . In contrast to the local-spin-density result the self-interaction-corrected formalism yields correctly an antiferromagnetic semiconducting ground state as found experimentally. The band gap of 2.1 eV and spin magnetic moment of  $0.66\mu_B$  compare favorably with experimental values. The bonding properties are correctly described proving that the SIC LSDA is also capable of describing the properties that have been correctly predicted within LSDA.

The failure of the local-spin-density-approximation (LSDA) to describe such strongly correlated materials as  $\text{La}_2\text{CuO}_4$  and transition-metal oxides is partially blamed on the electron self-interaction. Recently it has been shown that the self-interaction-corrected (SIC)-LSDA theory leads to correct antiferromagnetic ground states, in good agreement with experiment, for the 3d monoxides<sup>1,2</sup> and also for  $\text{La}_2\text{CuO}_4$ .<sup>3</sup> In contrast, the wave-vector-dependent spin susceptibility, calculated on the basis of the LSDA paramagnetic band structure of  $\text{La}_2\text{CuO}_4$ , has turned out to be two to three times too small for the transition to the antiferromagnetic state to occur.<sup>4</sup> A very detailed analysis of the various contributions to the spin susceptibility led us to the conclusion that the Cu *d* bands are not sufficiently localized within the LSDA picture, leading to gross underestimation of the intraband and interband transitions. However, these bands could be localized further within the SIC-LSDA scheme, and this was the original motivation for this study.

It is a paradox of the LSDA that it gives an adequate description of the bonding<sup>5</sup> and structural properties<sup>6</sup> of  $\text{La}_2\text{CuO}_4$  although the ground state itself is not correctly predicted.<sup>7</sup> Therefore, one should investigate whether the SIC-LSDA formalism is capable of providing a more consistent story, namely, to provide both the correct ground state and good description of the lattice constant. A future objective would be to apply the SIC-LSDA scheme to a Sr-doped compound to explore whether it can correctly describe the metallic nature of its ground state. For this our present study forms a rather essential starting point. Finally, it is of interest to see whether our results, based on a very different implementation of the SIC-LSDA formalism, support the findings of Svane.<sup>3</sup>

In this paper we study the electronic structure of  $\text{La}_2\text{CuO}_4$  by means of an *ab initio* band-structure scheme, self-interaction-corrected-linear-muffin-tin-orbital-atomic-sphere approximation (SIC-LMTO-ASA),<sup>2</sup> taking into account the self-interaction correction to the LSDA, and implemented within the standard LMTO-ASA

band-structure method.<sup>8</sup> As has already been mentioned, our implementation of the SIC-LSDA scheme differs substantially from the cluster approach of Svane and Gunnarsson<sup>1</sup> and is described in more detail in Ref. 2.

The SIC-LSDA Hamiltonian has the form

$$H_{\alpha}^{\text{tot}} \varphi_{\alpha}(\mathbf{r}) = [H^{\text{LSDA}} - \delta V_{\alpha}(\mathbf{r})] \varphi_{\alpha}(\mathbf{r}) = \sum_{\alpha'} \varepsilon_{\alpha\alpha'} \varphi_{\alpha'}(\mathbf{r}), \quad (1)$$

where  $H^{\text{LSDA}}$  is the usual LSDA Hamiltonian and

$$\delta V_{\alpha}(\mathbf{r}) = 2 \int \frac{|\varphi_{\alpha}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}^{\text{LSDA}}[|\varphi_{\alpha}(\mathbf{r})|^2, 0] \quad (2)$$

is the self-interaction correction to the usual LSDA potential and  $V_{\text{xc}}^{\text{LSDA}}$  is the LSDA exchange-correlation potential. The Lagrange multipliers  $\varepsilon_{\alpha\alpha'}$  ensure the orthogonality of the  $\varphi_{\alpha}(\mathbf{r})$  functions. In order to find the solution of the SIC-LSDA equations [defined by Eq. (1)] we employ the unified Hamiltonian concept.<sup>9</sup> It not only secures the orthogonality of both self-interaction-corrected and non-self-interaction-corrected orbitals, without a need for evaluating the Lagrange multipliers matrix, but also provides all self-interaction-corrected and non-self-interaction-corrected solutions from the same matrix diagonalization. However, at every iteration of the self-consistency (SCF) cycle, the following set of equations

$$\langle \varphi_{\alpha} | \delta V_{\alpha} - \delta V_{\alpha'} | \varphi_{\alpha'} \rangle = 0 \quad (3)$$

has to be satisfied, for every pair  $\alpha, \alpha'$ , in order to ensure the absolute minimum of the total energy for the mutually orthogonal orbitals with optimal degree of localization. These equations follow from the requirement that the SIC-LSDA energy functional is stationary under unitary transformations among the occupied orbitals and are often referred to as the localization criterion,<sup>9,10</sup> since they take care that the orbitals possess the optimal degree of localization for the total energy to become minimum. Therefore, in the SIC-LMTO-ASA band-structure

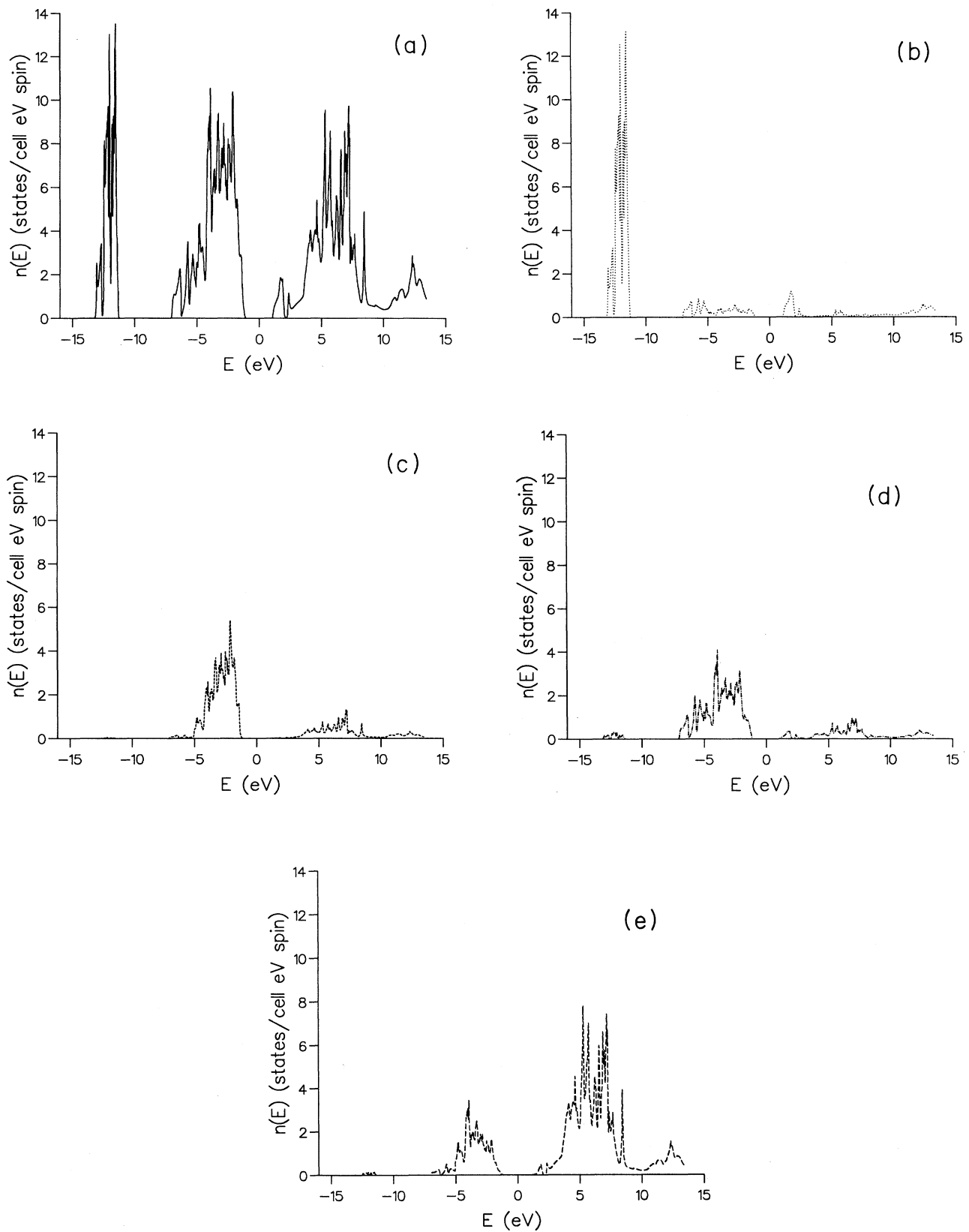


FIG. 1. SIC-LSDA density of states for  $\text{La}_2\text{CuO}_4$ : (a) the total density of states; (b) the Cu contribution to the total density of states; (c) the apex (out-of-plane) oxygen contribution; (d) the planar (in-plane) oxygen contribution; (e) the La contribution.

scheme one has to employ a two-level SCF cycle to reach convergence for both the total energy and wave functions.

As in the case of oxides,<sup>2</sup> we have applied the SIC only to the occupied Cu *d* states, five majority spin states, and four minority spin states. We have concentrated on the antiferromagnetic solutions and performed our calculations for the base-centered orthorhombic structure with 14 atoms per unit cell. Nonspherical contributions to the potential have not been considered, and the Wigner-Seitz cells have been approximated by spheres. With respect to the basis functions we have only included *s*, *p*, and *d* muffin-tin orbitals on Cu and La sites and *s* and *p* muffin-tin orbitals on the oxygen sites, and no empty spheres have been considered. Moreover, as in the case of the oxides we have employed the local approximation and have expanded the localized orbitals around central unit cell only.

Our *ab initio* results for the total density of states and its decomposition into Cu, planar (in-plane) oxygen, apex (out-of-plane) oxygen, and La contributions are presented in Fig. 1. The first thing to notice is a substantial band gap of 2.1 eV. This value compares favorably with the experimental gap of 2.0 eV.<sup>11</sup> One expects that including *d* muffin-tin orbitals on the oxygen sites will slightly reduce the present value of the band gap. In the case of transition-metal oxides, this reduction was of the order of 0.2–0.3 eV.<sup>2</sup> Note that although the band gap occurs between the non-SIC bands, the effect of the SIC is present through orthogonalizing these sets of band states to the SIC states.

The width of the valence band is about 6 eV. The top of this valence band is of predominantly oxygen character, hybridizing substantially with La states. Since the major effect of the SIC is to pull the occupied Cu *d* bands well below the valence band, they are not noticeably present at the top of the valence band. It appears that both kinds of oxygen atoms contribute with equal weights at the top of the valence band. The bottom of the conduction band is of predominantly Cu *d* character, however, there are some contributions from both the in-plane oxygen and La to the lowest unoccupied peak in the density of states. The La states are predominantly unoccupied, except for those hybridizing with the oxygen valence bands. Unexpectedly, the position of the occupied Cu *d* peak obtained within this approximate ground-state theory is in very good agreement with the position of the experimentally observed *d*<sup>8</sup> satellite at –12.5 eV.<sup>12</sup> Similar, favorable comparisons with experimental findings can be made for other features of the present density of states. Also, it is rather gratifying to see that our results are in good agreement with those of Svane,<sup>3</sup> in spite of a very different methodology employed and a smaller basis set used in the present calculation. The value of the spin magnetic moment of  $0.66\mu_B$  is rather high compared to the experimental value of  $0.4\mu_B$ ,<sup>13</sup> but again one would expect it to be reduced if *d* muffin-tin orbitals are placed on oxygen sites and *f* muffin-tin orbitals on La sites.

In Fig. 2, we have shown the dependence of the total energy on the unit-cell volume. We see that the theoretic-

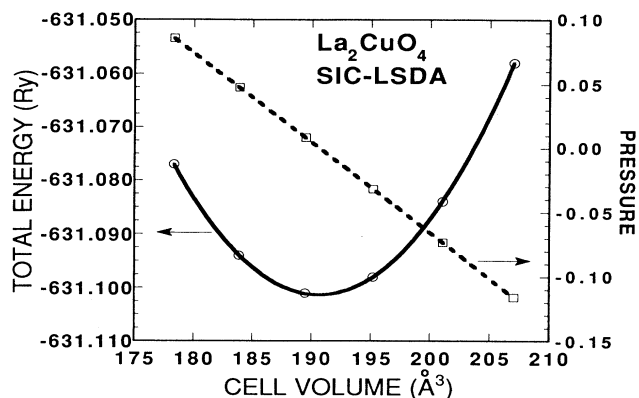


FIG. 2. The dependence of the SIC-LSDA total energy and pressure on the cell volume. The circles are the calculated total energies, the squares the calculated pressures, and the solid and dashed lines are cubic fits through the data points. The experimental cell volume is  $189.480 \text{ \AA}^3$ .

cal equilibrium volume ( $190.684 \text{ \AA}^3$ ) is within 0.6% of the experimental value ( $189.480 \text{ \AA}^3$ ). We obtain a bulk modulus of 1.33 mbars (1.25 mbars in the LSDA).<sup>5</sup> As in the case of LSDA, the SIC-LSDA provides an adequate description of the bonding properties of  $\text{La}_2\text{CuO}_4$ . This means that the SIC-LSDA scheme can describe both localization and unit-cell volume. In previous work<sup>14</sup> we speculated that, in spite of the wrong ground state, the LDA was still able to describe the bonding properties because this involved La and O atoms. We validate this speculation since the electronic structure resulting from these chemical components does not change substantially in going from the LSDA to the SIC-LSDA and hence the theoretical lattice constant hardly changes. To summarize to this point we would like to stress good agreement of our results with previous calculations and with experiment, if one can take the liberty to compare this approximate ground-state theory with high-energy spectroscopies.

We also find that the band gap remains roughly constant at 2.1 eV when changing the lattice constant from –2% to +3% of the experimental value. As the volume is changed both the bottom of the conduction band and the top of the valence band move in unison. This is presumably because both occupied and unoccupied states around the band gap are similar in character. Since the electronic structure in the vicinity of the band gap does not change much, we also find a small change ( $0.01\mu_B$ ) in the magnetic moment as a function of volume.

Finally, the LSDA-SIC results for the antiferromagnetic state can also shed some light on the search for spin fluctuations<sup>4</sup> in a hypothetical paramagnetic state with amplitudes large enough to drive the system into an antiferromagnetic phase transition or to bring it near to such a state. The LDA approach failed badly in this respect<sup>4</sup> because the contribution of the intraband transitions within band 17 (the only band crossing the Fermi level) in the body-centered-tetragonal (bct) structure turned out to be too small. This band has an appreciable width of 3 eV

which makes the wave-function coefficients strongly  $\mathbf{k}$  dependent. This, in turn, leads to small matrix elements because of the small wave-function overlap between occupied  $(\mathbf{k}, E)$  states and unoccupied  $(\mathbf{k}+\mathbf{q}, E+\omega)$  states. Within the SIC-LSDA, this band will most likely become substantially flatter. This happens as follows. One would SIC per spin four of the five Cu  $d$  bands for paramagnetic  $\text{La}_2\text{CuO}_4$ . The effect of the SIC would be to pull these bands well below the bottom of the valence band and to make them much more localized. The Cu  $d$  band crossing the Fermi energy, although not self-interaction

corrected, would be influenced by the SIC through orthogonalization to the very localized, self-interaction corrected, Cu  $d$  bands and hence would also become much flatter. Such a flat band could then drive the instability from the paramagnetic state to the antiferromagnetic state with stable and sizable magnetic moments at the Cu sites, as found in the present study.

This work was partially supported by a grant from the British Council and the German Academic Exchange Service.

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