VOLUME 68, NUMBER 12 PHYSICAL REVIEW LETTERS 23 MARCH 1992

Electronic Structure of La_2CuO_4 in the Self-Interaction-Corrected Density Functional Formalism

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(Received 16 December 1991)

The electronic structure of tetragonal La_2CuO_4 is calculated in the self-interaction-corrected (SIC) local spin density (LSD) approximation. In contrast to LSD, the SIC-LSD approach reveals the experimentally observed antiferromagnetic and semiconducting ground state. The energy gap is 1.04 eV and of indirect charge-transfer character, and the Cu moment is $0.47\mu_B$. The valence-band top states have about equal weight on the in-plane and out-of-plane O atoms. This region is dominated by O states not coupling to the Cu *d* states, but with a significant component of O states having Cu *d*-like symmetry.

PACS numbers: 71.25.Tn, 71.50.+t, 75.20.Hr

With the discovery of superconductivity in the copper oxide systems large efforts have been made to understand the electronic properties of these materials [1]. Electronic band-structure calculations of the basic La_2CuO_4 and $YBa_2Cu_3O_6$ compounds using the local spin density (LSD) approximation to density functional theory (DFT) fail in predicting their antiferromagnetic and semiconducting ground state [1], but describe the cohesive properties and phonon frequencies rather well [2]. The situation resembles that of the Mott insulating 3*d* monoxides MnO, FeO, CoO, and NiO, which are known to be wide-gap insulators but in LSD theory appear as metals (FeO and CoO) or small-gap semiconductors (MnO and NiO) [3]. Recently, it was demonstrated that much better agreement with experiments is reached for the 3*d* monoxides provided the self-interaction of each electron is subtracted [4]. The origin of the failure of LSD theory can be traced back to the mean-field character of the Kohn-Sham equations [5,6], by which the same potential is used to describe both valence and conduction electrons. Consequently, when DFT in the LSD approximation is taken one step beyond its formal justification, and the Kohn-Sham one-electron eigenenergies are used for comparison with experiments, there will be only minor differences between addition and removal energies. In particular, for Mott localized systems, the separation between electron and hole excitations—being of the order of the on-site Coulomb interaction *U* [7]—is missed.

The self-interaction-corrected (SIC) LSD approximation [8] provides a scheme by which the localization of electron states may be described [5]. Applied to the 3*d* monoxides, the SIC shifts the *occupied d* states down significantly, essentially by *U*, but leaves the *unoccupied d* states largely unaltered. This mechanism leads to the formation of large gaps of charge-transfer character in the 3*d* monoxides in agreement with experiment [4]. It is likely that the Cu-O superconductors, at least in their pure phases, have properties similar to those of the 3*d* monoxides, which motivates the present study of tetragonal La_2CuO_4 in the SIC-LSD approximation.

In the SIC-LSD approximation a localized electron moves in a potential, which consists of the usual mean-field-type LSD potential plus a correction for the electron's self-interaction, which erroneously is included in the LSD part:

$$[-\Delta + V_\alpha(\mathbf{r})]\Psi_\alpha(\mathbf{r}) = \epsilon_\alpha \Psi_\alpha(\mathbf{r}) + \sum_{\alpha' \neq \alpha}^{\text{occ}} \lambda_{\alpha,\alpha'} \Psi_{\alpha'}(\mathbf{r}) \,, \qquad (1)$$

$$V_\alpha(\mathbf{r}) = V^{\text{LSD}}(\mathbf{r}) - 2\int \frac{|\Psi_\alpha(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d^3r' - \mu_{\text{xc}}^{\text{LSD}}(|\Psi_\alpha(\mathbf{r})|^2) \qquad (2)$$

(atomic Rydberg units). In Eq. (1) there appears a set of Lagrange multipliers, $\lambda_{\alpha,\alpha'}$ ($\epsilon_\alpha \equiv \lambda_{\alpha,\alpha}$), to ensure orthonormality among the occupied orbitals. In Eq. (2) the second and third terms on the right-hand side represent the self-Hartree and self-exchange plus correlation interactions. For an extended state the self-interaction vanishes. In the study of atoms [8] and small molecules [9] it has been demonstrated that the SIC-LSD eigenenergies ϵ_α in Eq. (1) are closer to physical removal and addition energies than the corresponding LSD eigenvalues; i.e., Eq. (1) in fact is also a better approximation to the quasiparticle equation than the Kohn-Sham equations of LSD theory. Pederson and co-workers in addition found that diagonalizing the λ matrix (instead of taking just the diagonal elements) improves further the agreement with physical removal energies, and they proved that a Koopman theorem exists for the corresponding orbitals [9]. Here we follow their approach to obtain the removal and addition energies of La_2CuO_4. For a periodic solid this restores the Bloch picture; i.e., a hole is delocalized: From Eq. (1) it follows that $\lambda_{\alpha,\alpha'} = \langle \Psi_{\alpha'} | -\Delta + V_\alpha | \Psi_\alpha \rangle$, so that the on-site λ's may be interpreted as the energy of a localized hole and the off-diagonal λ's as hopping amplitudes. It is important to stress, though, that SIC LSD remains an approximate theory for the ground state, and much of the multiplet structure and final-state effects relevant in photoemission experiments may not be properly described.

The solution of the SIC equations is done iteratively [4]. We apply the linear-muffin-tin-orbital method in the tight-binding representation [10]. Partial waves of *s*, *p*, and *d* character (plus *f* for La) are included in all spheres, which include empty spheres [11]. The localized states are optimized in real space, and are well confined within a cluster of sixteen tetragonal units; i.e., they decay to zero over less than ~4 lattice constants. Identical localized states are assumed on all Cu atoms (apart from alternating spins); i.e., the crystal unit cell is face-centered orthorhombic. Strict orthogonality of all orbitals is imposed. The crystal potential (both the LSD part and the SIC part) is assumed spherically symmetric inside all spheres. No correction for sphere overlap is included.

The following picture of the La_2CuO_4 ground state emerges (Figs. 1-3): On all Cu atoms there are nine localized *d* orbitals, which energetically (due to the self-interaction correction) appear below the O *p* bands. The O *p* states are itinerant and completely filled with a gap to the lowest conduction state, which is likewise itinerant and essentially made up of the unoccupied Cu *d* states. Covalency effects reduce the self-consistent antiferromagnetic Cu moment from $1\mu_B$ to $0.47\mu_B$, which compares favorably with the experimental value of $0.4\mu_B$ [12]. Figure 1 shows the O *p* bands of La_2CuO_4 in the SIC-LSD approximation. The minimum gap is 1.04 eV and indirect. The valence-band top is located at the *H* point $(-\pi/2a,\pi/2a,0)$, while a second valence-band maximum is found 0.05 eV lower at $\frac{3}{8}(\pi/a,\pi/a,0)$. Neither of these states has the symmetry of a Cu *d* orbital. The conduction-band minimum is found at $(\pi/a,0,0)$. The minimum direct gap is 1.57 eV and also found in the neighborhood of $(\pi/a,0,0)$, while the gap at *H* is 1.63 eV. The total O *p* band width is 6.2 eV. The occupied Cu *d* states are not shown in Fig. 1 but appear ~12 eV below the valence-band top as two flat bands of width 0.3 eV and exchange split by 0.6 eV. In the LSD approximation, La_2CuO_4 is a nonmagnetic metal, with a valence-band width of 7.6 eV.

Figure 2 shows the density of states as calculated in the SIC-LSD approximation. Similar to the LSD results [1], the in-plane O states (O I) are spread over a wider range than the out-of-plane O states (O II), which contribute significantly to the upper ~2 eV of the valence bands. The very top of the valence bands has about equal proportions of O I and O II character. The covalency effects are evident from the rather large La projected density of states in the O bands, which reflects tails of O *p* states sticking into the large La spheres. The real La-derived states are located in the conduction bands. Since the self-interaction pulls the occupied Cu states below the O *p* band, only little Cu admixture is found in the O *p* band. Most distinct are the peaks at −2.7 and −4.2 eV, which are due to minority $d_{x^2-y^2}$ orbitals forming nonbonding and bonding states with the O *p* orbitals. The matching $d_{x^2-y^2}$ antibonding state, of course, constitutes the lowest

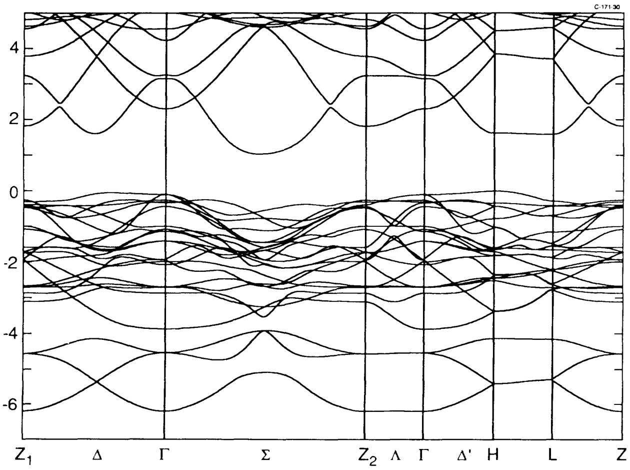

FIG. 1. SIC-LSD band structure of La_2CuO_4 along symmetry lines [Brillouin zone (units π/a): Z_1 (1,1,0)≡Z_2 (2,0,0)≡*Z* (0,0,*a*/*c*), *H* $(\frac{1}{2},-\frac{1}{2},0)$, *L* $(\frac{1}{2},-\frac{1}{2},a/c)$].

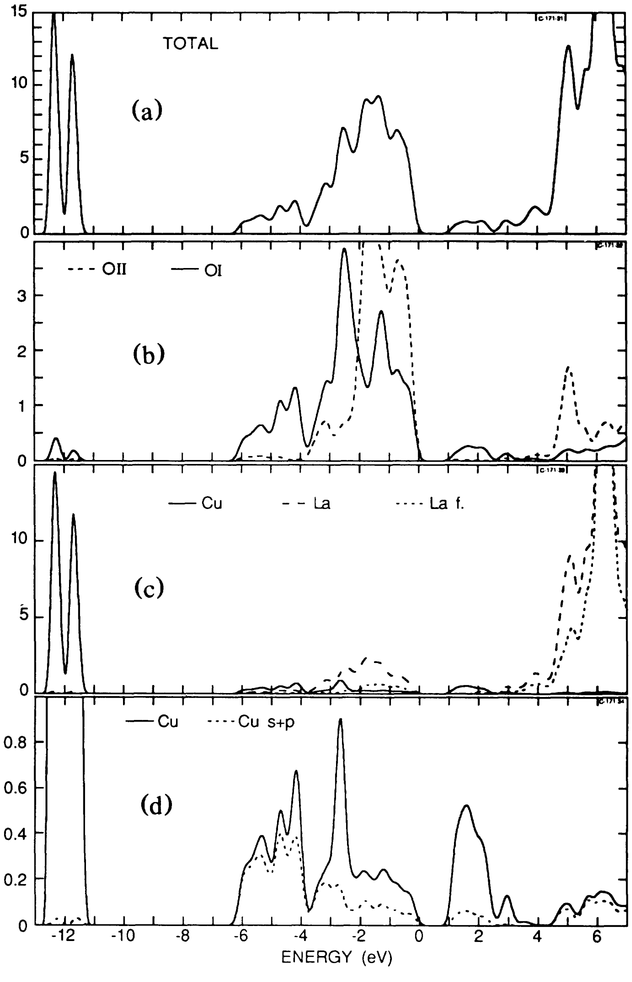

FIG. 2. SIC-LSD density of states of La_2CuO_4 in electrons per eV and formula unit and spin. (a) Total; (b) in-plane O (solid) and out-of-plane O (dashed curve) projected density of states (DOS); (c) Cu (solid curve) and La (dashed curve) projected DOS. The La *f* component in the conduction bands is shown by the dotted curve. (d) Cu total and non-*d* projected DOS. Note the different scales.

conduction band.

With the reservation that the present calculation does not describe all the details of the experimental situation, it is interesting to compare the theoretical density of states of Fig. 2 with photoemission experiments. The Cu d states at -12 eV in Fig. 2 match the position of the Cu d^8 satellite seen experimentally [13] at -12.5 eV, and the O p valence bands as calculated in the SIC-LSD approximation also seem to agree better with experiment than the corresponding LSD density of states. Thus, the O p derived bands in the top panel of Fig. 2 are seen to cause a major bell-shaped structure in the region of 0–4 eV below the valence-band edge and a tail towards larger binding energies. The O p density of states is maximal at -1.5 eV. Experimentally, the O p derived structure has a similar form with a width of 4.5 eV and the peak maximum located at -2.8 eV below the Fermi level [13]. A shoulder observed in experiment 1.7 eV below the primary peak may match the theoretical structure at -2.7 eV, which from Fig. 2 is seen to derive from in-plane O and Cu. This is in accord with the experimental observation that the primary O p band peak is more pure O p than the shoulder [13]. For the unoccupied states we first note that the experimental gap of La_2CuO_4 is 2 eV [14] in comparison with the present gap of 1.04 eV. This $\sim 50\%$ error is similar to what is encountered in LSD theory of most semiconductors. The calculated La-derived states are the La f bands at 6.4 eV above the valence-band edge and the La d shoulder around 5 eV. Experimentally, these features are observed at 8.7 and 5.8 eV [15], which—given a 1 eV general offset error in the theory for the conduction states—are in good agreement with the present calculations.

From the calculations we may extract some of the key parameters often used in models set up to describe superconductivity in (doped) La_2CuO_4. Thus, we identify the on-site Coulomb energy U with the difference in diagonal λ's [cf. Eq. (1)] for the highest occupied and lowest unoccupied Cu d state, which with the aforementioned interpretation of the λ's correspond to the definition $U = E(d^{10}) + E(d^8) - 2E(d^9)$ before hybridization effects are included [7]. This gives $U = 10.4$ eV. Similarly, the charge-transfer energy Δ is defined as the difference between λ for the unoccupied d orbital and the centroid of the O p λ's, which gives $\Delta = 1.1$ eV. Finally, we obtain the exchange splitting $\Delta_x = 0.5$ eV as the difference between majority-spin and minority-spin λ's. Hybridization effects are important in shifting the unoccupied d orbital upwards by 2.7 eV, i.e., effectively causing the semiconducting gap. Hybridization also shifts down the occupied d states by 0.2 eV, so that the *effective* Coulomb energy read off from Fig. 2 as the splitting between the two Cu d peaks becomes $U^{\mathrm{eff}} = 13.3$ eV [16].

In Fig. 3 the O p states are projected onto O states of d-like symmetry around a Cu atom. There is little spin dependence of the t_{2g}-like projected density of states, which simply spreads out over the entire O p band region. For the (x^2-y^2)-like orbital the spin-down weight falls in the lower half of the valence bands and matches the Cu peaks of Fig. 2; i.e., they are due to bonding and nonbonding states hybridizing with the unoccupied Cu $d_{x^2-y^2}$ orbital. The spin-up O (x^2-y^2)-like state, on the other hand, mixes into the upper half of the valence band with a distinct nonbonding peak at -2.7 eV and a somewhat broader antibonding peak at the valence-band top (the matching bonding state being Cu $d_{x^2-y^2}$ dominated and situated at -12 eV). The $(3z^2-1)$-like state has most of its weight in the upper 2-eV region with a significant shift at the valence-band maximum of the spin-down component relative to the spin-up component. Thus, a significant d-like O p character enters into the valence-band top of La_2CuO_4. On the other hand, comparing Figs. 2 and 3, it is clear that also the O p degrees of freedom not considered in Fig. 3 (i.e., those combinations of O p orbitals which do not form d-like symmetry

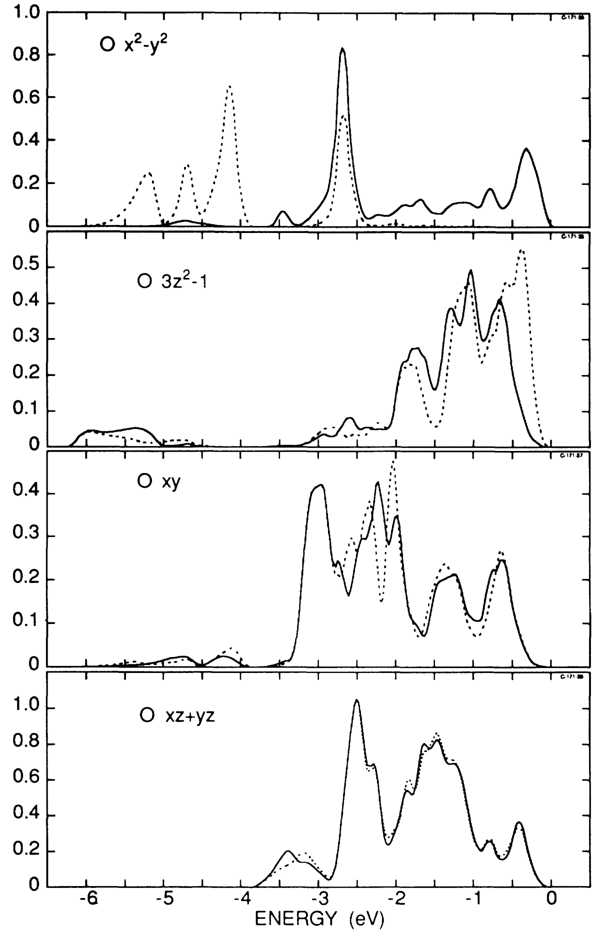

FIG. 3. SIC-LSD density of states of La_2CuO_4 projected onto O p states of d-like symmetry. Solid curve, spin up, and dashed curve, spin down, relative to a net spin-up Cu atom. Units as in Fig. 2.

states) contribute significantly in the entire valence-band region. In particular, a large non-*d*-like contribution enters the top valence structure. This has important implications for doped La_2CuO_4. On doping, the uppermost valence states will be emptied, i.e., the holes will reside predominantly on O sites, in accordance with experiment. The holes will, however, be neither entirely of *d*-like symmetry nor strictly confined to the basal CuO_2 planes. Therefore, these results suggest that model studies of the superconductivity in doped La_2CuO_4 in fact should incorporate all O degrees of freedom.

In summary, we have presented calculations of the electronic structure of La_2CuO_4 in the SIC-LSD approximation. The correct antiferromagnetic and semiconducting ground state is reproduced in this approximation, in contrast to the conventional LSD approximation. Good quantitative agreement with experiment is found for the Cu magnetic moment as well as for the energy gap and other electron excitation energies. The SIC-LSD approach is quite generally applicable to systems with localized states. The accuracy of the scheme needs to be tested in future investigations. In particular, for the $YBa_2Cu_3O_{6+\delta}$ compounds it is of interest to see if the SIC-LSD approximation, on the one hand, predicts the semiconductivity for $\delta=0$ and, on the other hand, preserves the successes of the LSD approximation in calculations of total energies and Fermi surface of the $\delta=1$ compound.

Many stimulating discussions with O. Gunnarsson as well as critical comments on the present manuscript by him and N. Christensen are gratefully acknowledged.

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[1] W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[2] R. E. Cohen, W. E. Pickett, and H. Krakauer, Phys. Rev. Lett. **62**, 831 (1989); **64**, 2575 (1990); C. O. Rodriguez, A. I. Lichtenstein, I. I. Mazin, O. Jepsen, O. K. Andersen, and M. Methfessel, Phys. Rev. B **42**, 2692 (1990).

[3] O. K. Andersen, H. L. Skriver, H. Nohl, and B. Johansson, Pure Appl. Chem. **52**, 93 (1979); K. Terakura, A. R. Williams, T. Oguchi, and J. Kübler, Phys. Rev. Lett. **52**, 1830 (1984); Phys. Rev. B **30**, 4734 (1984).

[4] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).

[5] A. Svane and O. Gunnarsson, Phys. Rev. B **37**, 9919 (1988); Europhys. Lett. **7**, 171 (1988).

[6] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[7] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[8] A. Zunger, J. P. Perdew, and G. L. Oliver, Solid State Commun. **34**, 933 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[9] M. R. Pederson, R. A. Heaton, and C. C. Lin, J. Chem. Phys. **80**, 1972 (1984); **82**, 2688 (1985); M. R. Pederson and C. C. Lin, J. Chem. Phys. **88**, 1807 (1988).

[10] O. K. Andersen, O. Jepsen, and D. Glötzel, in *Highlights of Condensed Matter Theory*, International School of Physics "Enrico Fermi," Course LXXXIX, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985), p. 59.

[11] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988). We use $S=2.48$, 1.98, 3.50, and 2.25 a.u. for the radius of the Cu, O, La, and empty spheres, respectively.

[12] D. Vaknin, S. K. Sinha, D. E. Moneton, D. C. Johnson, J. Newsam, C. R. Safinya, and H. E. King, Phys. Rev. Lett. **58**, 2802 (1987).

[13] Z. Shen, J. W. Allen, J. J. Yeh, J.-S. Kang, W. Ellis, W. Spicer, I. Landau, M. B. Mable, Y. D. Dalichaouch, M. S. Torikachvili, J. Z. Sun, and T. H. Geballe, Phys. Rev. B **36**, 8414 (1987).

[14] J. M. Ginder, R. M. Roe, Y. Song, R. P. McCall, J. R. Gaines, E. Ehrenfreund, and A. J. Epstein, Phys. Rev. B **37**, 7506 (1988).

[15] Y. Gao, T. J. Wagener, J. H. Weaver, A. J. Arko, B. Flandermeyer, and D. W. Capone, Phys. Rev. B **36**, 3971 (1987).

[16] In a calculation, where the nonspherical part of the SIC potential is taken into account, we find very similar results: $E_{\rm gap}=0.84$ eV, $m=0.42\mu_B$, $U=8.6$ eV, $\Delta=0.9$ eV, $U^{\rm eff}=11.6$ eV.