Electronic structure of high-temperature superconductors

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The electronic energy bands, local densities of states, and valences have been calculated for $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$, with a tight-binding model fitted to previous calculations for La_2CuO_4. Strong d-state peaks, predicted about 5 eV above the Fermi energy for La, Y, and Ba, should be observable in inverse photoemission, electron energy-loss spectroscopy, and final-state photoemission experiments.

Since the discovery of high-temperature superconductivity,[1,2] there has been rapid experimental progress. As yet, however, there is no confirmed theory. Here we present calculations of the electronic structures of $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ in the one-electron approximation, using a simple tight-binding Hamiltonian.

The band structures of La_2CuO_4 and $YBa_2Cu_3O_7$ have been previously calculated by Mattheiss and Hamann,[3,4] Freeman and co-workers,[5,6] Oguchi,[7] and Takegahara, Harima, and Yanase.[8] As will be seen below, we find that a tight-binding model[9] very nearly reproduces the results of these more complicated calculations, provided that one includes the unoccupied d states on La, Y, and Ba. We also find that the tight-binding parameters are transferable from the La compound to the 1:2:3 material. The advantage of a simple tight-binding description is that it provides a convenient starting point for further theoretical studies in various directions, such as models of superconductivity[10,11] and calculations of material properties.[12,13]

The model employed here includes the valence p and s orbitals of O and the d and s orbitals of all the metal atoms. There are thus 34 orbitals per chemical unit for La_2CuO_4 and 64 for $YBa_2Cu_3O_7$. Since the d states of La, Y, and Ba are unoccupied, one is tempted to neglect them. However, they appear to be required for a good description of charge transfer. (We find that La, Y, and Ba lose substantially more electronic charge when their d states are neglected.) On the other hand, the f states of La, Ba, and Y appear to be relatively unimportant,[8] so they are omitted. It appears to be a good general principle that the accuracy of a tight-binding model is improved if unoccupied d states near the Fermi energy are included.[14]

The "atomic energies" ε_s, ε_p, and ε_d for O, La, Sr, Y, and Ba were simply taken from the table of Harrison,[15] with ε_d taken to have the same value for Y and Sr and for La, Ba, and Lu. The interatomic matrix elements $V_{ss\sigma}$, etc., together with ε_s and ε_d for Cu, were determined by fitting the band structures of Refs. 3, 5, 7, and 8 for La_2CuO_4, and were then carried over to $YBa_2Cu_3O_7$ without modification. The interatomic matrix elements are defined in Ref. 15 as

$$V_{ll'm} = \eta_{ll'm} \frac{\hbar^2}{m_e d^2} \quad (l, l' = s \text{ or } p) \tag{1}$$

and

$$V_{ldm} = \eta_{ldm} \frac{\hbar^2 r_d^{3/2}}{m_e d^{7/2}} \quad (l = s \text{ or } p) . \tag{2}$$

The matrix element varies with the indicated inverse power of the interatomic distance d, and is characterized by a strength η. The size of the d orbital interaction is characterized by r_d. We obtain $\eta_{ss\sigma} = -1.1$, $\eta_{sp\sigma} = 0.9$, $\eta_{sd\sigma} = -1.6$, $\eta_{pd\sigma} = -2.5$, and $\eta_{pd\pi} = 1.4$; also $r_d = 0.95$ Å for Cu and 1.6 Å for the other metal atoms. (Since r_d for the other metal atoms has a relatively minor effect, we simply retained the value of Ref. 15, and adjusted r_d only for Cu.) The remaining parameters are listed in Table I. The replacement $La_2 \rightarrow La_{2-x}Sr_x$ was made in the virtual crystal approximation, i.e., by simply letting $\varepsilon_s(La) \rightarrow (1 - x/2)\varepsilon_s(La) + (x/2)\varepsilon_s(Sr)$. Since $\varepsilon_s(Sr) \approx \varepsilon_s(La)$, this is a good approximation in the present context. It also follows that the electronic states are virtually identical to those of La_2CuO_4 for the same crystal structure, and the only effect of the Sr is to remove x electrons per chemical unit.

We originally included second-neighbor interactions, such as O—O, but found that the optimum value of each such interaction was zero. This is fortunate, since a nearest-neighbor model is much more convenient in most applications.

The crystal structure of $La_{1.85}Sr_{0.15}CuO_4$ was taken from experiment,[16] but the doubling of the unit cell and small orthorhombic distortion were ignored for simplicity, as in Refs. 3, 5, 7, and 8. (It is not hard to perform the calculations for a larger or orthorhombic unit cell, but the band structure of Fig. 1 would have a complicated appearance. The small displacements associated with the distortions below about 200 K,[16] although fundamentally significant, would have an imperceptible effect in the

TABLE I. "Atomic energies" in eV.

	Cu	O	La	Sr	Y	Ba
$\varepsilon_d(\varepsilon_p)$	−14	(−14)	−6.6	−6.8	−6.8	−6.6
ε_s	−12	−29	−4.9	−5.0	−5.5	−4.5

present calculations.) The orthorhombic crystal structure of $YBa_2Cu_3O_7$ was taken from Ref. 16.

Our calculated energy bands for $La_{1.85}Sr_{0.15}CuO_4$ are shown in Fig. 1, with the conventional labeling of the symmetry points[3,17] and the zero of energy shifted to E_F. Comparison with the previous calculations[3,5,7,8] shows the same general behavior. The valence bandwidths at the ΔU midpoint and at X are 7.0 and 9.7 eV, compared with 6.5 and 9.4 eV in Ref. 3. The single prominent $Cu(d)-O(p)$ antibonding state protruding above E_F at X overlaps the lowest-lying conduction band by 0.9 eV, compared with 1.0 eV in Refs. 3 and 5, and 0.6 eV in Ref. 8. There are, of course, minor differences; for example, the highest occupied states along the line ΔU are about 0.5 eV nearer E_F in the more complicated calculations, but the most important features are in remarkably good agreement. The bands are found to have almost two-dimensional character,[3,5] with little variation in the k_z direction, perpendicular to the CuO_2 planes.

Figure 2 shows the local densities of states for this material, with $O(1)$ and $O(2)$ respectively labeling the in-plane and out-of-plane oxygen sites. (The calculation employed 24 special points[18] in the irreducible part of the Brillouin zone, with a 0.2 eV broadening.) The total density of states at E_F is 1.2 states/eV cell, compared with previous calculations ranging from 1.3 states/eV cell[3] to 2.1 states/eV cell.[7] Since $O(2)$ is more weakly bonded to Cu, it is more ionic, with a sharper p state peak below E_F. The $Cu(d)$ and $O(p)$ states, which have nearly the same energy, are almost fully occupied. The electron occupancy n_i for each atomic site i is determined by a weighted average over the Brillouin zone sample points of

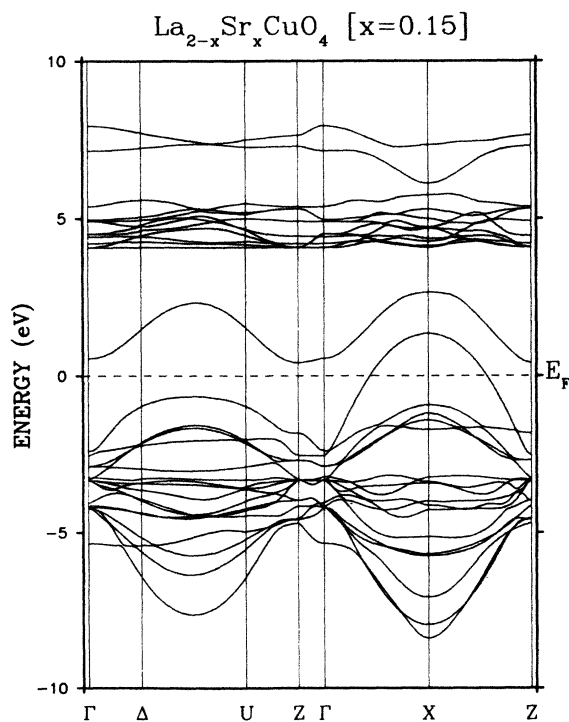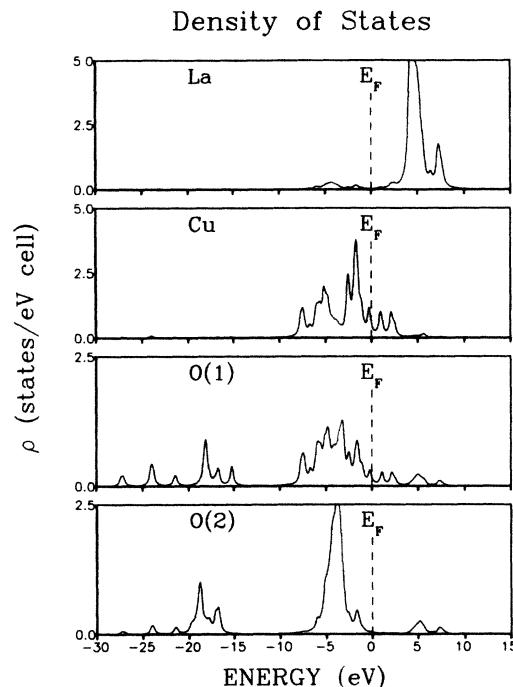$$n_i = 2 \sum_{\alpha, E \leq E_F} |\psi_i^\alpha(E)|^2 , \qquad (3)$$

Density of States

FIG. 2. Local densities of states for $La_{1.85}Sr_{0.15}CuO_4$.

where $\psi_i^\alpha(E)$ is the component of the eigenfunction corresponding to valence orbital α on atom i, and two electrons occupy each state up to E_F. We find that Cu has very nearly 10 electrons, $O(1)$ about 7.1, and $O(2)$ about 7.5. One might interpret the first number as corresponding to approximately zero $Cu(d)$ holes.

If we define the valence Δn to be the number of electrons lost by the atom when it is bonded in the solid, then $\Delta n = +1.0$, -1.1, and -1.5 for Cu, $O(1)$, and $O(2)$, respectively, as indicated in Table II. Since all bonds have some covalent character, Δn is expected to be substantially less than the customary formal valence of chemistry. For example, a valence calculation which we performed for cubic Cu_2O (cuprite) gives a Δn of $+0.24$ for Cu and -0.48 for O, compared with the formal valences Cu^{1+} and O^{2-}. Similarly, a calculation for monoclinic CuO (tenorite) yields $Cu^{0.79+}$ and $O^{0.79-}$, compared with the formal valences Cu^{2+} and O^{2-}. If we were to interpret the formal valence as roughly twice the calculated valence Δn (up to the maximum reasonable value), then Table II

FIG. 1. Electronic energy bands for $La_{1.85}Sr_{0.15}CuO_4$.

TABLE II. Valence Δn.

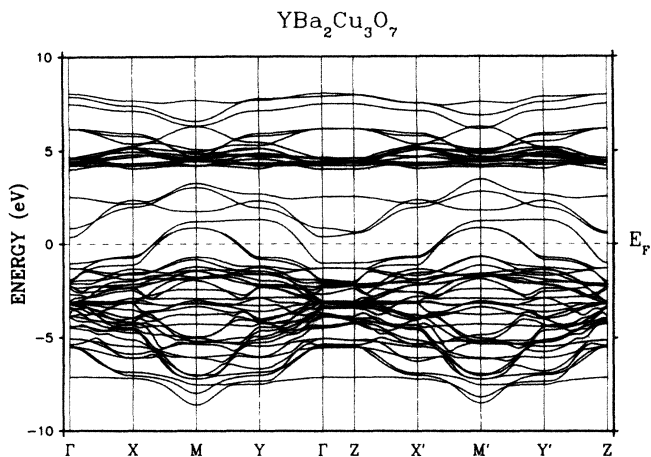| $La_{1.85}Sr_{0.15}CuO_4$		$YBa_2Cu_3O_7$	
Cu	+1.02	Cu(2)	+0.98
		Cu(1)	+1.34
O(1)	−1.12	O(1)	−1.12
		O(2)	−1.09
		O(3)	−1.11
O(2)	−1.51	O(4)	−1.21
La	+2.12	Y	+1.77
Sr	+1.12	Ba	+1.44

$YBa_2Cu_3O_7$

FIG. 3. Energy bands for $YBa_2Cu_3O_7$.

gives Cu^{2+}, O^{2-}, La^{3+}, and Sr^{2+}. The exact balancing of these formal valences in La_2CuO_4, as in $SrTiO_3$ and re-lated materials, suggests a structural stability resulting largely from the charge transfer.[15,16] The divalent nature of Sr, of course, indicates the presence of holes in $La_{2-x}Sr_xCuO_4$.

Figure 3 shows our calculated energy bands for $YBa_2Cu_3O_7$, with the labeling of the symmetry points defined in Fig. 4. The valence bandwidths at M and M' are 9.7 and 9.6 eV, compared with 8.9 eV in Ref. 6. The bands protruding above E_F at M and Y peak at 1.5 and 1.6 eV above E_F, compared with 1.7 and 1.8 eV in Ref. 6. The near equivalence of the left- and right-hand sides, and the small variation along ΓZ, demonstrate the two dimen-sionality of the electronic structure.[4,6] For this triple perovskite structure, there are now three antibonding $Cu(d)-O(p)$ bands protruding above E_F at M and M'. Two of them are nearly the same as the corresponding band for the La compound in Fig. 1, being associated with the CuO_2 planes adjacent to the Y; but one has essentially no dispersion along MY, being associated with CuO chains in the y direction.

The local densities of states for this 1:2:3 material are shown in Figs. 5 and 6. (We used 64 special points in the
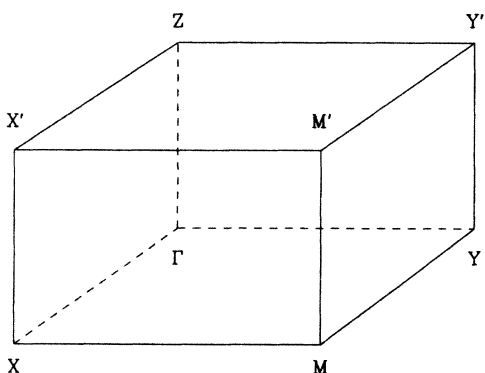

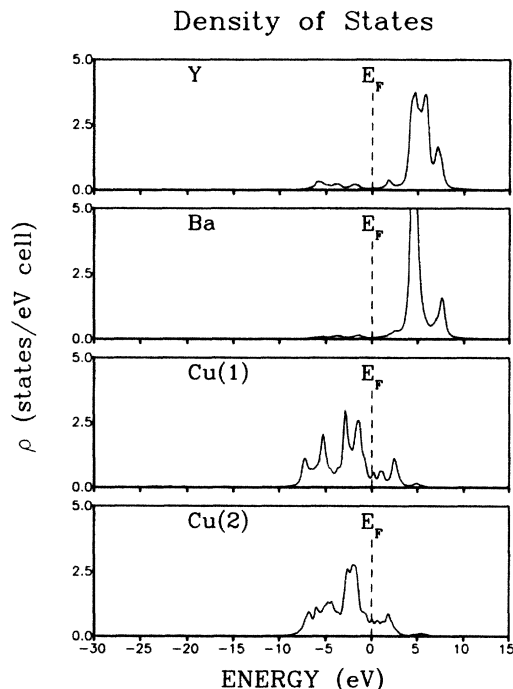FIG. 4. Symmetry points of Fig. 3. ΓY is parallel to the CuO chains.

Density of States

FIG. 5. Local densities of states for $YBa_2Cu_3O_7$, metal atoms.

irreducible part of the Brillouin zone, and 0.2 eV broaden-ing.) The total density of states at E_F is 3.2 states/eV cell, compared with 3.0 states/eV cell in Ref. 4 and 3.4 states/eV cell in Ref. 6. $Cu(1)$ and $O(1)$ refer to the CuO chains; $Cu(2)$, $O(2)$, and $O(3)$ to CuO_2 planes, as in Ref. 16; and $O(4)$ to the out-of-plane oxygens. The features
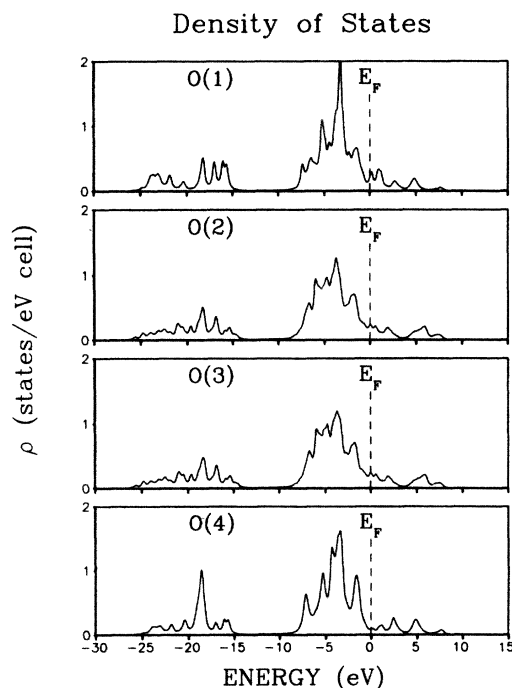
Density of States

FIG. 6. Local densities of states for $YBa_2Cu_3O_7$, oxygen atoms.

are very similar to those for the La compound. For both materials, there is a rather low density of states at the Fermi energy.[4,6] Strong d-state peaks are predicted a few eV above the Fermi energy for Y and Ba in $YBa_2Cu_3O_7$, for La/Sr in $La_{2-x}Sr_xCuO_4$, and for the corresponding metal atoms in related high-temperature superconductors. These peaks should be observable in electron energy-loss spectroscopy[19] and final-state photoemission spectroscopy.[20]

The calculated valences Δn are again given in Table II. Notice that Δn is approximately $+1$ for Cu in the CuO_2 planes, just as in the La compound, but $\Delta n = +1.34$ for the CuO chains. One might interpret this result as corresponding to $\frac{1}{3}$ Cu(d) hole per chemical unit with no doping. This difference in valences should be observable in photoemission on high-quality, single-crystal surfaces. If we again were to interpret the formal valence as very roughly twice Δn, Table II would give Cu^{2+} (planes), Cu^{3+} (chains), O^{2-}, Y^{3+}, and Ba^{2+}, so that the formal valences again neatly cancel in $YBa_2Cu_3O_7$.

In summary, we have calculated the electronic structures of the most typical members of the two known classes of high-temperature superconductors. The present results, obtained with a simple tight-binding model, are in good agreement with those obtained in more complicated calculations.[3-8] A remarkably simple picture emerges, with conclusions that can be tested experimentally.

After the original submission of the present paper, three papers appeared with inverse photoemission measurements indicating unoccupied d bands for both $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-y}$ which are in approximate agreement with those predicted here.[21-23] Since the f-electron states have little influence on the other states and on the charge transfer,[8] we have omitted them from the present model; the strong features associated with unoccupied f states in the experimental spectra are consequently also omitted. Finally, we mention that Onellion, Margaritondo, and co-workers have observed the dispersion of the antibonding Cu—O band along ΓM for $YBa_2Cu_3O_7$.[24]

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[4]L. F. Mattheiss and D. R. Hamann, Solid State Commun. **63**, 395 (1987).

[5]J. Yu, A. J. Freeman, and J.-H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).

[6]S. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).

[7]T. Oguchi, Jpn. J. Appl. Phys. **26**, L417 (1987).

[8]K. Takegahara, H. Harima, and A. Yanase, Jpn. J. Appl. Phys. **26**, L352 (1987).

[9]An earlier version of the present model for $La_{1.85}Sr_{0.15}CuO_4$ was given in B. A. Richert and R. E. Allen, in *Proceedings of the 18th International Conference on Low Temperature Physics,* edited by Y. Nagaoka [Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 989 (1987)].

[10]B. A. Richert and R. E. Allen, in *Proceedings of the 18th International Conference on Low Temperature Physics,* edited by Y. Nagaoka [Jpn. J. Appl. Phys. 26, Suppl. 26-3, 2047 (1987)].

[11]B. A. Richert and R. E. Allen, in *Proceedings of the Drexel International Conference on High Temperature Superconductivity,* edited by S. Bose and S. Tyagi (World Scientific, Singapore, 1988), p. 149.

[12]B. A. Richert and R. E. Allen, in *Proceedings of the American Vacuum Society, Topical Conference on Thin Film Processing and Characterization of High-T_c Superconductors,* edited by J. M. E. Harper, R. J. Colton, and L. C. Feldman, AIP Conference Proceedings No. 165 (Americal Institute of Physics, New York, in press).

[13]B. A. Richert and R. E. Allen, in *High Temperature Super-conductors,* edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller [Mater. Res. Soc. Proc. (to be published)].

[14]D. A. Papaconstantopoulos (private communication); O. F. Sankey (private communication).

[15]W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[16]D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987); R. J. Cava, A. Santoro, D. W. Johnson, and W. W. Rhodes, Phys. Rev. B **35**, 6716 (1987); T. Siegrist, S. Sunshine, D. W. Murphy, R. J. Cava, and S. M. Zahurak, Phys. Rev. B **35**, 7137 (1987), and references therein.

[17]A. W. Luehrmann, Adv. Phys. **17**, 1 (1968).

[18]D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

[19]Y. Chang, M. Onellion, D. W. Niles, R. Joynt, G. Margaritondo, N. G. Stoffel, and J. M. Tarascon, Solid State Commun. **63**, 717 (1987).

[20]G. Margaritondo and M. Onellion (private communications).

[21]T. J. Wagener, Y. Gao, J. H. Weaver, A. J. Arko, B. Flandermeyer, and D. W. Capone II, Phys. Rev. B **36**, 3899 (1987).

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

[23]J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi, and F. J. Himpsel, Phys. Rev. B **36**, 3967 (1987).

[24]N. G. Stoffel, Y. Chang, M. K. Kelly, L. Dottl, M. Onellion, P. A. Morris, W. A. Bonner, and G. Margaritondo, Phys. Rev. B (to be published). See also M. Onellion, Y. Chang, M. Tang, R. Joynt, E. E. Hellstrom, M. Daeumling, J. Seuntjens, D. Hampshire, D. C. Larbalestier, G. Margaritondo, N. G. Stoffel, and J. M. Tarascon (unpublished).