Quadruple perovskites $L'L''Ba_2Cu_2Ti_2O_{11}$ as good candidates for high-temperature superconductors: Role of oxygen defects

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The electronic structure and properties of $LaYBa_2Cu_2Ti_2O_{11}$, as a typical member of the $L'L''Ba_2Cu_2Ti_2O_{11}$ family, were determined by means of the full-potential linear muffin-tin method. From the results obtained it appears that $L'L''Ba_2Cu_2Ti_2O_{11}$ may be a good candidate for high-T_c superconductivity since its band structure at the Fermi energy is dominated by a quasi-two-dimensional Cu-O $dp\sigma$ band with a prominent van Hove singularity. We suggest that hole doping of about 0.6 holes per unit cell (or 0.3 holes per Cu-O layer) through mono- and/or divalent metal substitution for lanthanides may lead to an optimum T_c in these materials. The role of different structural imperfections on the T_c that apparently could be created in the process of chemical doping — oxygen impurities between the Cu-O layers and oxygen vacancies in the Ti-O plane — was also determined. We found that these likely structural imperfections are unfavorable for the creation of the superconducting state in these materials.

In the search for new and better high-temperature superconductors, many new families of layered perovskite structures have been discovered. One of them is the family of the quadruple perovskites $L'L''Ba_2Cu_2Ti_2O_{11}$ (L= lanthanide, Y). Gormezano and Weller[1,2] discovered the layered compound $Gd_2Ba_2Ti_2Cu_2O_{11}$; subsequently, other independent investigations have shown that substitution of other lanthanides for gadolinium was possible.[3–7] Recently, a comprehensive study of the crystal chemistry of $L_2Ba_2Cu_2Ti_2O_{11}$ (L = lanthanides) was carried out and in addition, layered materials with mixed lanthanide stoichiometries $L'L''Ba_2Cu_2Ti_2O_{11}$ were reported.[8] These materials satisfy some general conditions for the occurrence of high-temperature superconductivity: they contain complete CuO_2 planes and a ''charge reservoir'' consisting of a double perovskite structure composed of L', Ti, and O. Thus, they may have good promise to be superconductors if appropriate doping of CuO_2 planes is achieved. However, since recent attempts to substitute Gd by Ca in $Gd_2Ba_2Ti_2Cu_2O_{11}$ (Ref. 9) have not been successful, the question of whether it is possible to make these materials superconducting still remains open.

This paper addresses this question from the point of view of the electronic structure of one of those materials—$LaYBa_2Cu_2Ti_2O_{11}$—studied by means of the local-density approximation full-potential linear muffin-tin orbital method (FLMTO).[10–13] Starting from the band-structure results for ideal (i.e., defect free) $LaYBa_2Cu_2Ti_2O_{11}$, we investigate the role of several possible structural imperfections — interlayer oxygen impurities (p type) and oxygen defects (n type) in the ''charge reservoir.''

The average structure of $LaYBa_2Cu_2Ti_2O_{11}$ (Ref. 8) is tetragonal with the lattice parameters $a=3.8969$ Å and $c=15.716$ Å and belongs to a $P4/mmm$ space group, cf. Fig. 1. Atomic positions are listed in Table I. It was found[8] that Y almost exclusively occupies the eight-coordinate site between Cu-O planes. We label the oxygen positions in the following way: O(1) is located in La-O plane, O(2) in the Ti-O plane, O(3) is an ''apical'' oxygen with respect to Cu-O planes and O(4) together with Cu atoms form the Cu-O layers. We have performed calculations for the defect-free $LaYBa_2Cu_2Ti_2O_{11}$ structure, for the structure containing oxygen between the Cu-O planes and for a structure containing 50% of O(2) vacancies. The calculations were performed using the FLMTO method[10–13] in a spin-restricted scalar-relativistic mode with atomic Cu $3d^{10}4s^14p^0$, Ti $3d^24s^24p^0$, Y $4d^15s^25p^0$, Ba $6s^25p^65d^0$, La $6s^25p^65d^1$,

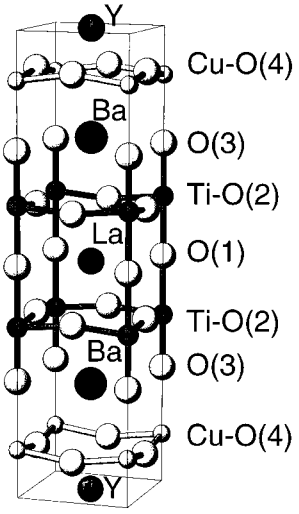

FIG. 1. Crystal structure of LaY $Ba_2Cu_2Ti_2O_{11}$.

TABLE I. Atomic coordinates (in units of the lattice constant) and muffin-tin (MT)-sphere radii for ideal $LaYBa_2Cu_2Ti_2O_{11}$ used in the FLMTO calculations ($a=7.3636$ a.u., $c/a=4.0331$) (Ref. 8).

Atom	x	y	z	R_{MT}, a.u.
Y	0.5	0.5	0.0	2.4
Ba	0.5	0.5	0.94	3.3
La	0.5	0.5	2.02	3.1
Cu	0	0	0.42	1.8
Ti	0	0	1.49	1.7
O(1)	0	0	2.02	1.9
O(2)	0.0	0.5	1.54	1.9
O(3)	0.0	0.0	1.02	1.64
O(4)	0	0.5	0.35	1.9

and O $2s^2 2p^4$ orbitals treated as valence band electrons and Cu $3s^2 3p^6$, Y $4p^6$, Ba $5p^6$ and Ti $3s^2 3p^6$ treated as semicore states (in a second energy window). We used a triple-κ basis set for each type of atom with angular momentum l up to 3 for Y, Ba, and La and up to 2 for the other atoms for $\kappa^2=-0.01$ Ry, and with l up to 1 for $\kappa^2=-1.0$ and -2.3 Ry. The charge density was calculated exactly in the muffin-tin spheres for angular momentum components up to $l=5$. The same l cutoff was used when interpolating in the interstitial region over Hankel functions with energies -1 and -3 Ry. The Brillouin-zone (BZ) integrations were carried out using an 84 k-point mesh.

In our discussion we will analyze the electronic structure of the ideal $LaYBa_2Cu_2Ti_2O_{11}$ and its changes related to crystal imperfections keeping in mind the common features of the electronic band structures of the known high-T_c superconductors. The most important seems to be the presence of a strongly hybridized Cu $3d$-O $2p$ derived band crossing the Fermi energy (E_F), and the presence of a van Hove saddle-point singularity (vHs) in the close vicinity of E_F,[14,15] which also appears to be favorable for superconductivity.

The FLMTO band structure of the *ideal* $LaYBa_2Cu_2Ti_2O_{11}$ in the vicinity of E_F along some symmetry lines in the simple tetragonal BZ is presented in Fig. 2, where $X=(\pi/a;0;0)$, $M=(\pi/a;\pi/a;0)$, $R=(\pi/a;0;\pi/c)$, and $A=(\pi/a;\pi/a;\pi/c)$. Surprisingly, the band structure in the vicinity of E_F is very simple and looks like a band structure typical to all Cu-O based high-T_c superconductors. That is, only the quasi-two-dimensional Cu-O derived free-electron-like $dp\sigma$ bands cross E_F. This feature of the band structure suggests by analogy with other Cu-O based high-T_c superconductors that the undoped material is expected to be a Mott-Hubbard insulator. Indeed, the temperature dependence of the electrical resistivity of isostructural (and isoelectronic) materials exibit semiconductor behavior.[1,2,9] The total and l-projected densities of states (DOS) for $LaYBa_2Cu_2Ti_2O_{11}$ are presented in Fig. 3. Again, as for all Cu-O based high-T_c superconductors, the only con-

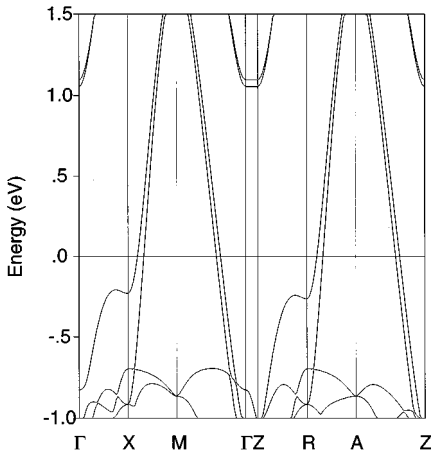

FIG. 2. FLMTO band structure of the ideal $LaYBa_2Cu_2Ti_2O_{11}$ structure in the Fermi energy region along some high-symmetry directions.

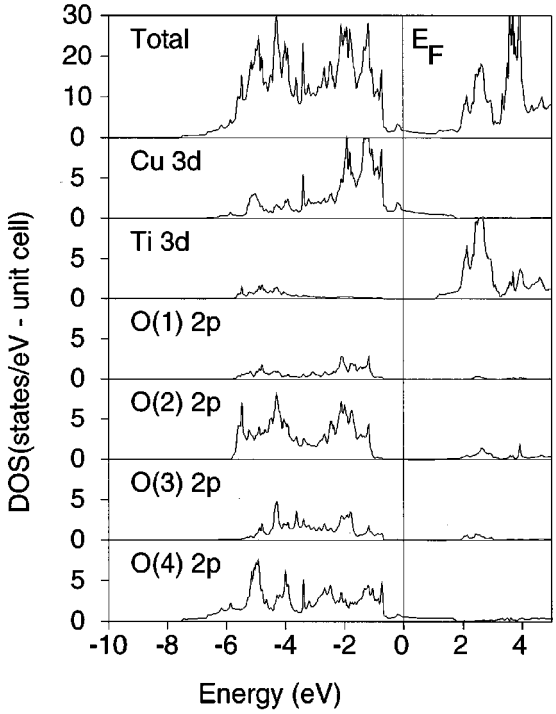

FIG. 3. Total and $l-$ projected DOS for ideal $LaYBa_2Cu_2Ti_2O_{11}$.

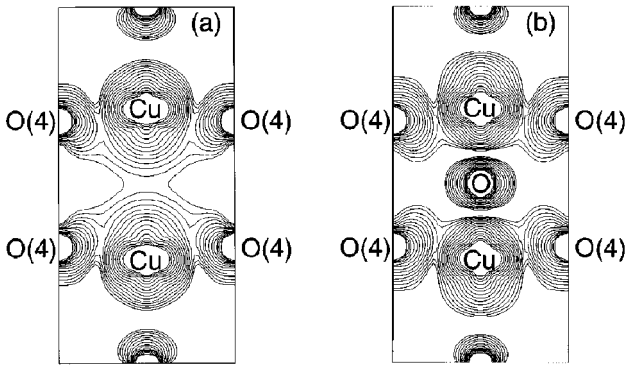

FIG. 4. Square of the wave function at the X point in the BZ normalized to two electrons per unit cell in the (010) plane for (a) ideal $LaYBa_2Cu_2Ti_2O_{11}$ and (b) $LaYBa_2Cu_2Ti_2O_{11}$ containing additional oxygen (O) between the Cu-O layers. Contours start from 10^{-3} e/a.u.^{3} and increase successively by a factor of $\sqrt{2}$.

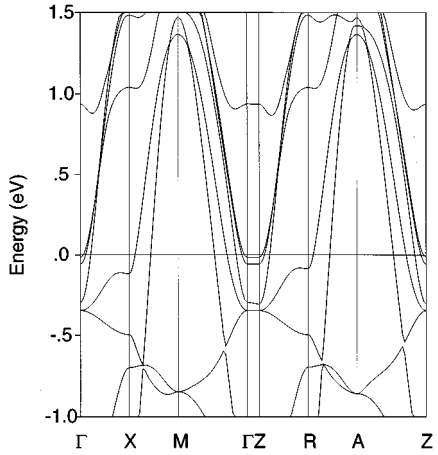

FIG. 5. FLMTO band structure in the Fermi energy region along some high-symmetry directions of the $LaYBa_2Cu_2Ti_2O_{11}$ containing additional oxygen between the Cu-O layers.

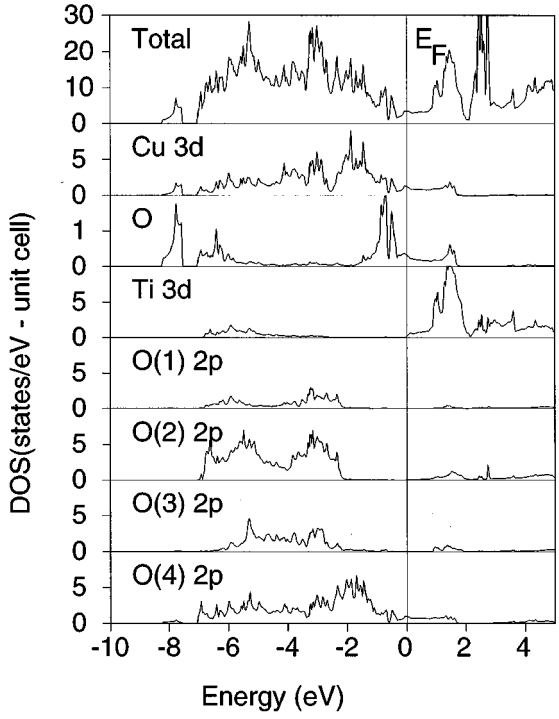

FIG. 6. Total and l-projected DOS for $LaYBa_2Cu_2Ti_2O_{11}$ containing additional oxygen between the Cu-O layers.

tribution to the DOS at the Fermi energy comes from the Cu $d-$ and O(4) $p-$ (in-plane oxygen) states. The prominent van Hove singularity is clearly seen on the DOS at 0.33 eV below E_F. The DOS composition at the E_F is also typical for high-T_c superconductors — it mainly consists of Cu $3d$ and O(4) $2p$ states. The two-dimensional character of the band can be clearly seen from the plot in the (010) plane of the square of the wave function at the X point in the BZ corresponding to the vHs [cf. Fig. 4(a)], which is mainly localized along the Cu-O planes. Thus, from these features of the band structure we may expect $LaYBa_2Cu_2Ti_2O_{11}$, and most probably other members of the $L'L''Ba_2Cu_2Ti_2O_{11}$ family (since their crystal structure and valence electron concentration are practically the same) to display superconductivity, if properly doped. If we associate the ''optimum doping'' with the position of the Fermi energy in the close vicinity of the vHs, which seems to be quite relevant,[14,15] we may predict the hole doping to be about $\sim$ 0.6 holes per unit cell, or $\sim$ 0.3 holes per Cu-O layer. Most likely such a doping can be achieved by substituting mono- or divalent atoms for Y and/or lanthanides.

Next we investigated the effect of two possible crystal defects which can strongly interfere with effective doping and the ''two dimensionality'' of Cu-O $dp\sigma$ bond: (i) an oxygen impurity incorporated between the Cu-O layers along the Cu-Cu bond and (ii) the oxygen [O(2)] vacancy in Ti-O planes. Figure 5 shows the band structure of $LaYBa_2Cu_2Ti_2O_{11}$ containing additional oxygen between the Cu-O layers. In conjunction with Fig. 6 that presents the total and l-projected DOS, one can see that the main differences from the ideal $LaYBa_2Cu_2Ti_2O_{11}$ are (i) the lowering of the antibonding part of the Ti $3d$ states down to E_F because of the change in electrostatic potential of the Cu-O layers and (ii) the appearance of new interlayer oxygen states at E_F. These oxygen states contribute heavily to the former Cu-O $pd\sigma$ band and change its character. Figure 4(b) presents the squared wave function at the same X point in the BZ as for the ideal $LaYBa_2Cu_2Ti_2O_{11}$. Although the states of the interlayer oxygen at this point in the BZ do not form any chemical bonding with states of the Cu-O layers, they contribute strongly to the band composition. It is interesting to note that this one extra oxygen per unit cell, which one can think would heavily dope the Cu-O $pd\sigma$ band by holes, does not significantly change the energy difference between the vHs and E_F. This suggests that the extra oxygen in between the Cu-O layers is mostly in its atomiclike state. Consequently, any doping coming from the ''charge reservoir'' would most probably first localize on that interlayer oxygen and prevent the $pd\sigma$ band from being optimally doped. Also, the incorporation of this extra oxygen apparently changes the two-dimensional character of the $pd\sigma$ band, which is thought to be responsible for the high-T_c properties of Cu-O layered ceramics. Thus, we can speculate on why the attempts to make $L'L''Ba_2Cu_2Ti_2O_{11}$ superconducting have failed so far. Most probably, in the process of doping some additional oxygen is incorporated between the Cu-O layers and this alters the character of the states at the E_F and destroys the main condition for high-T_c superconductivity.

Finally, we examined the electronic structure of LaY $Ba_2Cu_2Ti_2O_{11}$ containing 50% oxygen vacancies at the O(2) site. The band structure plotted in Fig. 7 shows that additional bands appear in the vicinity of E_F. From the total and l-decomposed DOS (Fig. 8), one can see that Ti d states shift down in energy and now contribute to the DOS at E_F. The nature of those states can be understood from their specific space localization. A detailed analysis of the charge distribution coming from these states shows that they are mainly localized in the region of the Ti-O plane.

Figure 9 shows the contour map of the square of the wave function associated with the topmost band below E_F at the X point in the BZ. The appearance of such ''vacancy states'' below E_F is caused by rearrangement of electron states around oxygen vacancies with a decisive role played by changes of wave functions of Ti atoms closest to the va-

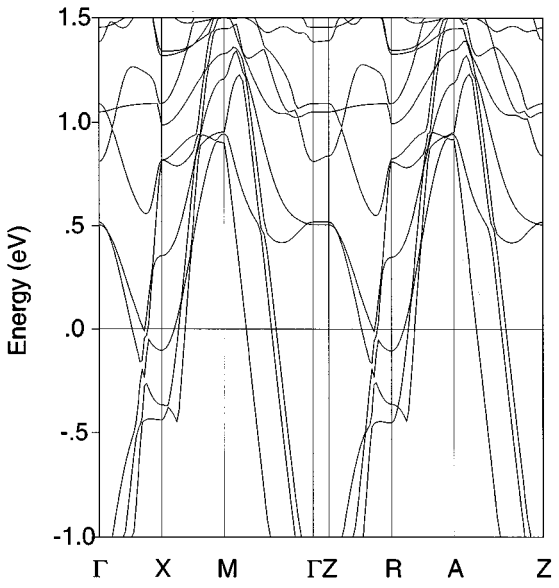

FIG. 7. FLMTO band structure in the Fermi energy region along some high-symmetry directions of the LaY $Ba_2Cu_2Ti_2O_{11}$ containing oxygen vacancies in the Ti-O layers.

cancy. Specifically, the appearance of an O(2) vacancy leads to the breakdown of direct Ti-O bonding and to the creation new Ti-Ti bonds through the vacancy region. This also was found to be a common feature of the electronic structure of carbides and nitrides of transition metals containing metalloid vacancies.[16] Such an analysis suggests that ''extra'' electrons created in the Ti-O layers by oxygen vacancies will not

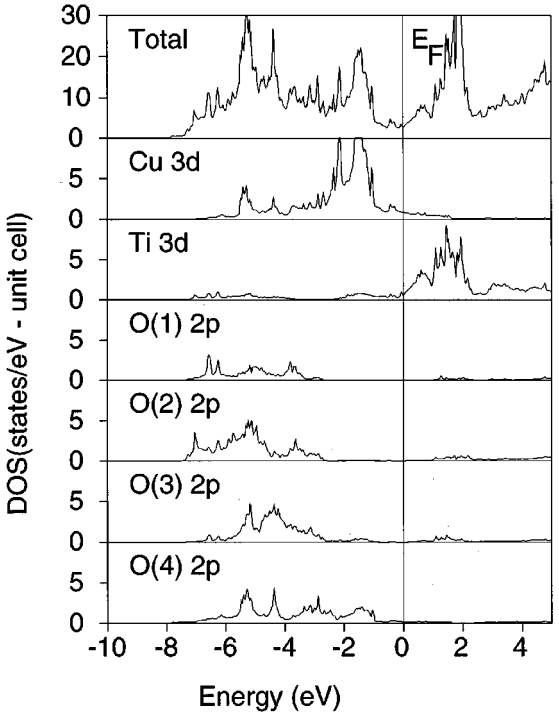

FIG. 8. Total and l-projected DOS for $LaYBa_2Cu_2Ti_2O_{11}$ containing oxygen vacancies in the Ti-O layers.

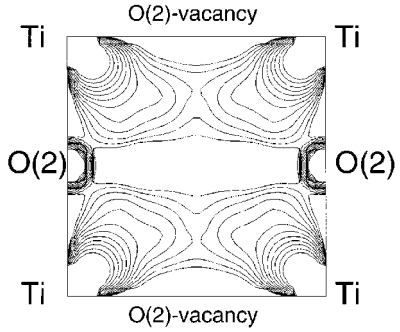

FIG. 9. Square of the wave function at the X point in the BZ normalized to two electrons per unit cell in the (001) Ti-O plane for $LaYBa_2Cu_2Ti_2O_{11}$ containing oxygen vacancies in the Ti-O layers. Contours start from 10^{-3} e/a.u.^{3} and increase successively by a factor of $\sqrt{2}$.

be able to move to the Cu-O layers and change the carrier concentration since they stay in the vicinity of O vacancies taking part in Ti-Ti bonding. It is also interesting to find the character of the electron states associated with Cu-O planes that lie close to E_F. At the X point in the BZ, the band closest to E_F of Cu-O(4) character was found at $\sim$ 0.5 eV below E_F. The square of the wave function of this band, presented in Fig. 10, is seen to differ dramatically from the character of the states in ideal $LaYBa_2Cu_2Ti_2O_{11}$ [Fig. 4(a)]. Thus, we should conclude that oxygen vacancies in the Ti-O plane are also not good for superconductivity since they (i) do not contribute to the doping ability of the ''charge reservoir'' and (ii) destroy the two-dimensional character of the Cu-O states at the Fermi energy.

To summarize, from FLMTO band structure calculations of $LaYBa_2Cu_2Ti_2O_{11}$ as a typical member of the $L'L''Ba_2Cu_2Ti_2O_{11}$ family we found, from the point of view of electronic structure, that the whole $L'L''Ba_2Cu_2Ti_2O_{11}$ family may be a good candidate for high-T_c superconductivity. Their band structure at E_F is dominated by a quasi-two-dimensional Cu-O $dp\sigma$ band with a prominent vHs. We suggest that hole doping of about 0.6 holes per unit cell (or 0.3 holes per Cu-O layer) through mono- and/or divalent metal

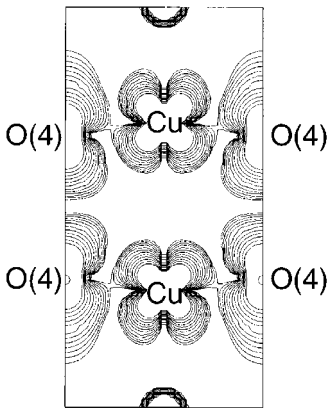

FIG. 10. Square of the wave function at the X point in the BZ normalized to two electrons per unit cell in the (010) Cu-O plane for $LaYBa_2Cu_2Ti_2O_{11}$ containing oxygen vacancies in Ti-O layers. Contours start from 10^{-3} e/a.u.^{3} and increase successively by a factor of $\sqrt{2}$.

substitution for lanthanides should lead to an optimum T_c in these materials. We have also investigated the role of different structural imperfections that are apparently created in the process of chemical doping (namely oxygen impurities between the Cu-O layers and oxygen vacancies in the Ti-O plane), and we have shown that they are unfavorable for the creation of superconducting state in these materials.

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