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Electronic structure of superconductors without apical oxygen: $Sr_2CuO_2F_2$, $Sr_2CuO_2Cl_2$, and $Ca_2CuO_2Cl_2$

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The electronic structures of $Sr_2CuO_2F_2$, $Sr_2CuO_2Cl_2$, and $Ca_2CuO_2Cl_2$ are investigated by means of the full-potential linear muffin-tin orbital method. As in other high-T_c cuprates, the electronic structures of these compounds display strong two-dimensional features including a low density of states at E_F and a simple Fermi surface of the form of a rounded square. A major Van Hove saddle-point singularity exists near the Fermi level. We predict the optimum superconductivity properties in these materials to occur when doped by 0.35–0.38 holes per unit cell.

I. INTRODUCTION

The recent discovery of superconductivity in $Sr_2CuO_2F_{2+\delta}$ (Ref. 1) and $(Ca_{1-x}Na_x)_2CuO_2Cl_2$ (Ref. 2) has opened a new class of superconducting compounds with the apical oxygen substituted by other elements (F, Cl). Although the superconducting temperature (T_c) found in these phases [46 K for $Sr_2CuO_2F_{2+\delta}$ and 26 K for $(Ca,Na)_2CuO_2Cl_2$] is not as high as for other high-T_c layered Cu-O superconductors, the new phases are of great interest because of the expectation that they can help improve our understanding of the nature of high-temperature superconductivity.

The purpose of this work is to investigate the role of the lack of apical oxygens on the band structure and density of states of the parent compounds $Sr_2CuO_2F_2$, $Sr_2CuO_2Cl_2$, and $Ca_2CuO_2Cl_2$ and their electronic properties which we correlate with varying degrees of "hole doping." We find that the electronic structures of these compounds display the same features as found in the high-T_c cuprates (strong two dimensionality, a low density of states, and a simple Fermi surface in the form of a rounded square). Since a major two-dimensional (2D) Van Hove saddle-point singularity (VHS) exists near E_F, we will assume, as in our previous papers,[3–5] that its position determines the optimum hole (or electron) doping level needed to achieve the highest possible T_c in a specific class of compounds. We will argue that $Sr_2CuO_2F_{2+\delta}$ with δ=0.6, which is the estimated composition synthesized by the authors of Ref. 1, turns out to be heavily overdoped and that proper doping may help achieve better superconducting properties, including higher T_c. Since the optimum doping level for $(Ca_{1-x}Na_x)_2CuO_2Cl_2$ (Ref. 2) is unknown so far, our theoretical investigation might be helpful in estimating this important parameter and in establishing common features of the electronic structure of high-T_c superconductors without apical oxygen in their structures.

II. CRYSTAL STRUCTURE AND METHOD

$Sr_2CuO_2Cl_2$ crystallizes in the well-known K_2NiF_4 structure with space group symmetry D_{4h}^{17} and lattice parameters a=3.975 Å and c=15.618 Å.[6] Although $Sr_2CuO_2F_{2+\delta}$ was found[1] to be an orthorhombic phase, we neglect its orthorhombicity (since the precise crystal structure has not been established[1]) in our calculations and also use an idealized K_2NiF_4 structure here with lattice parameters a=3.857 Å and c=13.468 Å. The lattice parameters for $Ca_2CuO_2Cl_2$ ($a \sim 3.86$ Å and $c \sim 15.1$ Å) were taken from Ref. 2. The idealized base-centered tetragonal (bct) unit cell used for our calculations is displayed in Fig. 1 and the atomic positions in the unit cell are listed in Table I.

The calculations were performed using the full-potential linear muffin-tin orbital (FLMTO) method[7] in a spin-restricted scalar-relativistic mode with atomic Cu $3d^{10}4s^1$, Sr $5s^24p^6$, Ca $5s^24p^6$, O $2s^22p^4$, F $2s^22p^5$, and Cl $3s^23p^5$ orbitals treated as valence band electrons and Cu $3s^23p^6$ and Sr $4s^2$ 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 2 for Cu, O, F, and Cl and up to 3 for Sr for $\kappa^2 = -0.01$ Ry, and up to 1 for $\kappa^2 = -1.0$ and -2.3 Ry. The charge density was calculated exactly in the muffin-tin spheres (radii are listed in Table I) for angular momentum components up to l=6. 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 a 646 k-point mesh (corresponding to $24 \times 24 \times 24$ divisions) in the $\frac{1}{16}$ irreducible wedge.

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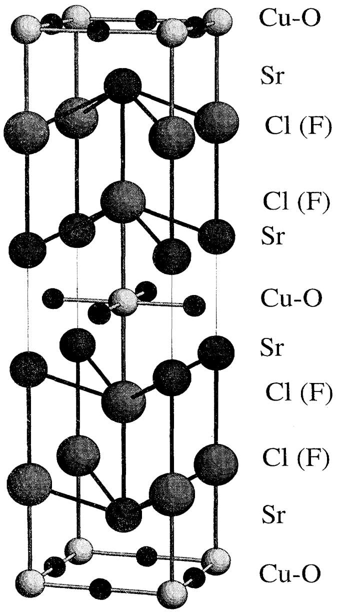


FIG. 1. Structure of $Sr_2CuO_2Cl_2$ and $Sr_2CuO_2F_2$ (simplified).

III. RESULTS

In order to simplify the interpretation of their band structures, we plot the FLMTO band structure results for these compounds in Fig. 2 along some symmetry lines in the simple tetragonal (not *bct*) Brillouin zone. The total and angular-momentum-projected densities of states (DOS) for the different atoms inside their MT spheres are displayed in Fig. 3.

The band structures of these compounds are very similar and have features common to all high-T_c cuprates. The lack of the apical oxygen has no effect on the states close to E_F. For all of them, a CuO_2-derived free-electron-like $dp\sigma$ antibonding band crosses the Fermi energy. It is exactly half-filled in the undoped case, indicating that the compounds must be antiferromagnetic insulators according to a Mott-Hubbard description. The prominent VHS derived from the Cu-O $dp\sigma$ band is seen at the X and R points in the BZ; cf. Fig. 2. For $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$, the VHS at the R point undoubtedly shows the features of an extended Van Hove singularity, the importance of which was discussed recently by Abrikosov.[8]

The densities of states for these compounds also look very similar. The only difference is, of course, in the energy positions of the Cl $3p$ and F $2p$ bands, with the former located deeper in energy. For all compounds, the

TABLE I. Atomic coordinates (in units of the lattice constant) and MT-sphere radii for $Sr_2CuO_2F_2$ and $Sr_2CuO_2Cl_2$ used in the FLMTO calculations.

Type	Atom	x	y	z	R_{MT} (a.u.)
$Sr_2CuO_2F_2$	Cu	0.0	0.0	0.0	1.82
a =7.322 a.u.	O	0.5	0.0	0.0	1.82
c/a=2.455	F	0.0	0.0	0.629	1.62
	Sr	0.5	0.5	0.463	3.14
$Sr_2CuO_2Cl_2$	Cu	0.0	0.0	0.0	1.92
a =7.512 a.u.	O	0.5	0.0	0.0	1.82
c/a=1.965	Cl	0.0	0.0	0.719	2.65
	Sr	0.5	0.5	0.424	3.10

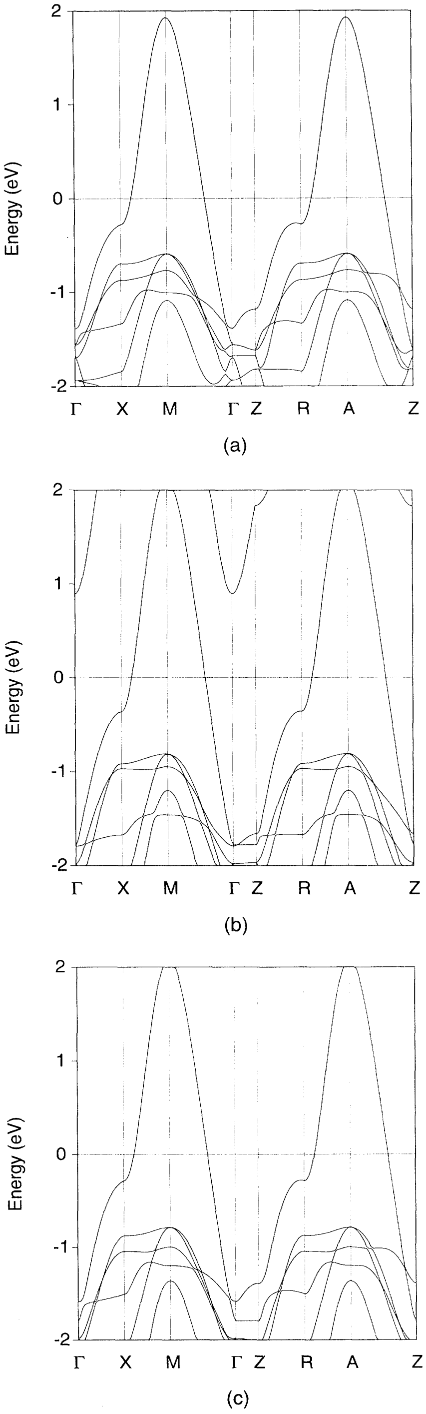
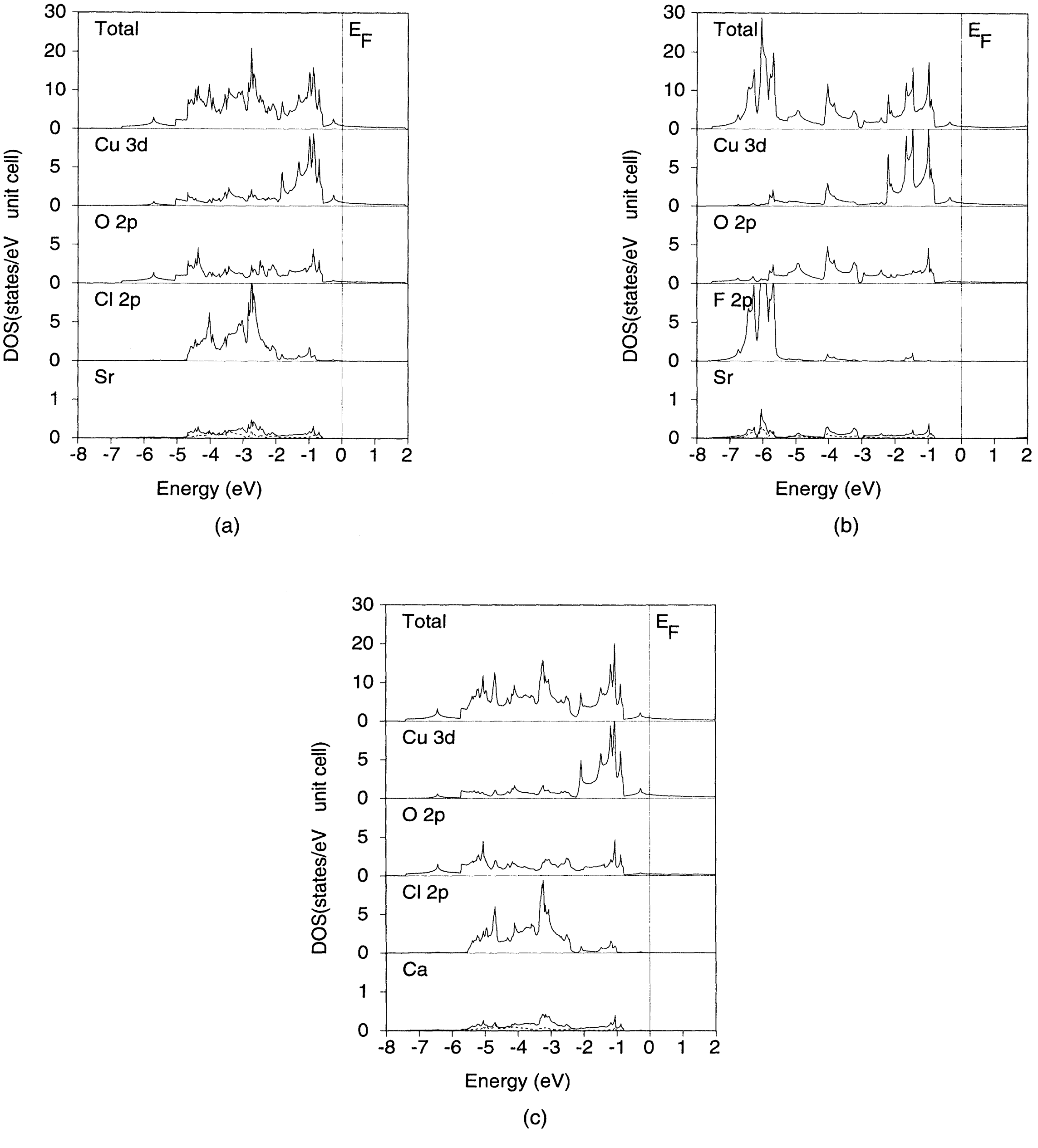


FIG. 2. FLMTO band structure of (a) $Sr_2CuO_2Cl_2$, (b) $Sr_2CuO_2F_2$, and (c) $Ca_2CuO_2Cl_2$ in the Fermi energy region.



(a)

(b)

(c)

FIG. 3. Total and projected DOS of (a) $Sr_2CuO_2Cl_2$, (b) $Sr_2CuO_2F_2$, and (c) $Sr_2CuO_2Cl_2$.

dominant feature near the Fermi level is a peak in the DOS caused by the VHS, which is found at −0.36 eV for $Sr_2CuO_2F_2$, at −0.27 eV for $Sr_2CuO_2Cl_2$, and at −0.28 eV for $Ca_2CuO_2Cl_2$ below the Fermi level. The total DOS in the Fermi energy region is shown in Fig. 4 for $Sr_2CuO_2Cl_2$. The values of the DOS at E_F and the energy corresponding to the VHS are listed in Table II. For the ideal structures, $N(E_F)$ for these compounds is about 1 state/(eV unit cell) which is the value (per Cu atom) typical for all high-T_c Cu-O materials. The projected Cu $3d$ and O $2p$ DOS also show a strong Cu-O hybridization

TABLE II. Total and l-decomposed DOS at E_F and at the position of the VHS for $Sr_2CuO_2F_2$ and $Sr_2CuO_2Cl_2$ in states/(Ry unit cell).

	Total DOS	Cu $3d$	O $2p$	F $2p$	Cl $3p$
$Sr_2CuO_2F_2$	10.6	6.1	2.7	0.1	—
at the VHS	27.3	16.4	4.6	0.6	—
$Sr_2CuO_2Cl_2$	12.7	7.0	3.3	—	0.4
at the VHS	33.3	18.5	5.8	—	2.7
$Ca_2CuO_2Cl_2$	11.6	6.6	2.8	—	0.3
at the VHS	26.1	15.4	4.6	—	1.7

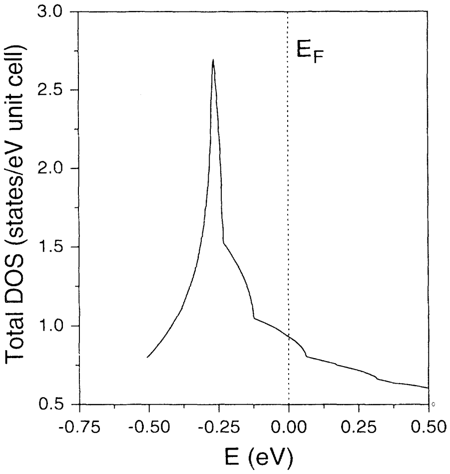


FIG. 4. Expanded total DOS in the vicinity of E_F for $Sr_2CuO_2Cl_2$.

at the Fermi level. If we assume that the VHS may play an important role in the high-T_c superconductivity, it is important to estimate the total DOS at the energy of the VHS; cf. Table II. As seen, the main contribution to the total DOS comes from the Cu 3d and O 2p orbitals and is almost 3 times larger than that at E_F for the undoped compound. Note also that the Cl 2p contribution to the DOS at the VHS for $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$ is considerably higher than that for $Sr_2CuO_2F_2$, but is still much smaller than the Cu and O contributions. As seen from Table II, the total DOS at the VHS increases from $Ca_2CuO_2Cl_2$ to $Sr_2CuO_2F_2$, which correlates well with the T_c enhancement. Note also that the total DOS reaches its maximum for $Sr_2CuO_2Cl_2$, which could indicate that the best value of T_c might be obtained for $Sr_2CuO_2Cl_2$, if properly doped.

The two-dimensional Cu-O band gives rise to a simple Fermi surface (FS). Figure 5 shows the FS for $Sr_2CuO_2Cl_2$ (it looks absolutely the same for the other compounds considered). It has the shape of a rounded square (as for the other single-Cu-O-layer high-T_c materials) and is practically undispersed along the Γ-Z direction. It drastically changes its shape when doping shifts the Fermi energy onto the VHS in which case the FS becomes pinched and touches the BZ boundaries.

As in our previous papers,[3–5] we correlate the optimum T_c value for a given compound with pinning of the VHS to the Fermi energy by appropriate doping (whether electrons or holes). Thus, we estimate the number of holes needed to hit the VHS to be about 0.38 holes for $Sr_2CuO_2Cl_2$ and $Sr_2CuO_2F_2$ and about 0.35 for $Ca_2CuO_2Cl_2$. It is interesting to note that these values coincide with the "optimum doping level" for the one-layer Hg-1201 compound.[5] This suggests that the optimum doping level might be an intrinsic property of the band structure of just the single Cu-O layer reflected as a universal value. The transition temperature of 46 K was achieved in $Sr_2CuO_2F_{2+\delta}$ for an estimated composition of $\delta=0.6$.[1] Providing that F is incorporated into the crystal as assumed,[1] we may conclude that the doping level of 0.6 holes is in a heavily overdoped regime. If correct, we may propose that a substantial increase of T_c is possible by removing the excess fluorine down to the level of $\delta \sim 0.38$. The observed doping level for $(Ca,Na)_2CuO_2Cl_2$ is estimated to be about 0.08 holes per Cu atom,[2] which is far below our theoretical optimum value. This may mean that (i) the authors have not reached the optimum doping level and hence that a further increase of T_c in $(Ca,Na)_2CuO_2Cl_2$ is possible, or (ii) their estimate of the number of holes needs to be improved.

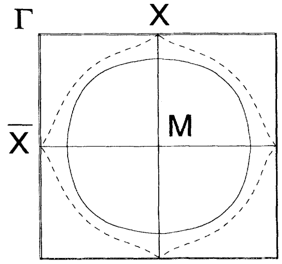


FIG. 5. Fermi surface $Sr_2CuO_2Cl_2$ for undoped case (solid line) and for an opimum doped case (dashed line).

Finally, if one considers the possibility of achieving superconductivity by monovalent metal substitutions for Ca in $Ca_2CuO_2Cl_2$ or Sr in $Sr_2CuO_2Cl_2$, we may propose from our results an optimum composition of $(M_{0.35-0.38}M'_{0.65-0.62})_2CuO_2X_2$, where M stands for a monovalent metal such as Na, K, ... and M' is Ca or Sr, and X stands for F or Cl. In such a case, from the total DOS at the VHS we can expect a higher T_c for $(M_{0.35-0.38}Sr_{0.65-0.62})_2CuO_2X_2$ rather than for the compounds considered.

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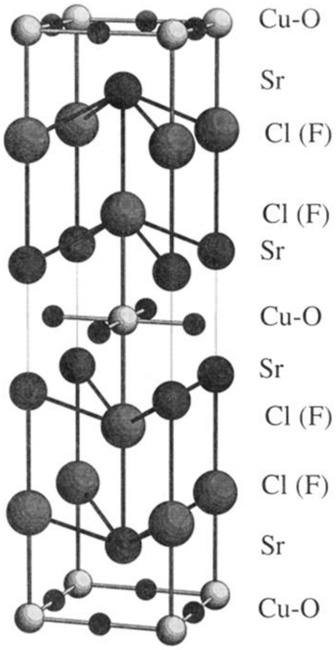

FIG. 1. Structure of $Sr_2CuO_2Cl_2$ and $Sr_2CuO_2F_2$ (simplified).