

# ***Ab initio* periodic approach to electronic structure and magnetic exchange in $A_2CuO_2X_2$ ( $A=Ca,Sr$ and $X=F,Cl$ ) high- $T_c$ superconductor parent compounds**

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The electronic structure of  $A_2CuO_2X_2$  ( $A=Ca, Sr$  and  $X=F, Cl$ ) compounds is investigated by means of the periodic unrestricted Hartree-Fock (UHF) method using the linear combination of atomic orbitals approach (LCAO). The relative stability of different alternative structures is discussed. All the systems are described as insulators with strong ionic character and well localized spin moments on the Cu atoms. The O 2*p* nature of the highest occupied bands is clear, supporting the charge transfer nature of this kind of narrow band systems; optical gaps are however, overestimated. The magnetic ordering of these materials is two dimensional in nature with almost independent antiferromagnetic  $CuO_2$  planes with  $J_c/J_1 \sim 10^{-3}$ . The in-plane nearest ( $J_1$ ) and next-nearest ( $J_2$ ) magnetic coupling constants are antiferromagnetic and much larger than the interplane interactions ( $J_c$ ), with  $J_2/J_1 \sim 0.02$ . The relative values of the magnetic constants are in qualitative agreement with available experimental results. None of the analyzed properties provide differences between the various compounds so relevant to limit the possible development of a superconducting phase. On the contrary, the close similarity between them suggest that kinetic limitations in the doping process can be responsible of the fact that no superconducting transition has been observed in  $Sr_2CuO_2Cl_2$  and in the  $T'$  phase of  $Sr_2CuO_2F_2$  and  $Ca_2CuO_2F_2$ .

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## I. INTRODUCTION

Since the discovery of the anomalous properties of high- $T_c$  superconducting cuprates (HTSC's), the crystal and electronic structure of these compounds had attracted considerable attention from the experimental point of view. In addition, the failure of the phonon mediated pairing mechanism proposed by Bardeen, Cooper, and Schrieffer (BCS) to account for the superconductivity in these systems was a new challenge to theorists to explain their properties.<sup>1-3</sup> Many theoretical models have been reported aimed to disclose the fundamental microscopic interactions governing the pairing mechanism in high- $T_c$  superconductors. The effective parameters appearing in the microscopic models can be extracted either from experiment or from theoretical calculations and a detailed analysis of the electronic structure of simple materials is necessary to disentangle the fundamental aspects common to all of them that are responsible for the appearance of a superconducting phase.<sup>2,4</sup>

HTSC's are ceramic materials that show as a common feature a layered crystal structure with well-defined  $CuO_2$  planes in which strong magnetic interactions give rise to a two-dimensional (2D) antiferromagnetic order ( $J_1 \sim -125$  meV) of the spin moments on the  $Cu^{2+}$  ions. It is widely accepted that these strong antiferromagnetic interactions in the  $CuO_2$  planes are at the origin of the fundamental mechanisms of superconductivity in these materials.<sup>1,2,5-7</sup> The pure, stoichiometric "parent" compounds are charge-transfer insulators with gaps between 1.5 and 2.0 eV that show a insulator-metal transition when doped. Light doping usually leads to a superconducting phase that evolves to a strange metallic phase for excess dopant concentrations.<sup>2,5</sup> It is well accepted that the  $CuO_2$  planes are the essential part of

a cuprate superconductor in which the extra mobile charges (holes or electrons) given by the other layers, usually called "charge reservoirs," move. The role of these charge reservoirs is to chemically control the number of mobile charges in the  $CuO_2$  planes and usually are considered as secondary or even irrelevant for the pairing mechanism.<sup>2,6,7</sup> Usually, the theoretical descriptions of HTSC's focus on the nature of the  $CuO_2$  planes and include the effect of the other layers in a very indirect way, or ignore them. However, specific questions on the interaction between the dopant and the charge reservoirs and the effect on the  $CuO_2$  planes are important to decide the reduction to the essential scheme supposed by the models. To address this kind of questions, it is important to be able to correctly describe the electronic structure of these materials, at least at a qualitative level, and to focus on the fundamental parameters governing the microscopic mechanisms of superconductivity and the relations that control their values. Hence, a systematic theoretical approach to the electronic structure of the simplest HTSC compounds whose physical properties exhibit a smooth variation from one system to the other would permit to develop a qualitative study to address most of these questions.

The monolayered cuprate compounds have simple structures and most of them have been extensively studied in the past years in their pure and doped phases. The family of oxyhalide compounds with formula  $A_2CuO_2X_2$  ( $A=Ca, Sr$  and  $X=F, Cl$ )<sup>8-20</sup> belongs to this class of simple cuprates which have also a smooth variation in their structural and chemical properties. This family is an optimal candidate to a theoretical research because its constituent ions are chemically simple (not trivalent lanthanides), have different structures without apical oxygens and have quite different superconducting behavior. Superconductivity has been found in

$\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  (Refs. 15,16), in  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  (Refs. 10,11), and also in the closely related compound  $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$ , which shows one of the highest known critical temperatures for a monolayered HTSC with  $\text{La}_2\text{CuO}_4$  structure.<sup>21</sup> However, the closely related compounds  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ,  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$  seem not to be superconducting for the available doping concentrations.<sup>8,17,18</sup> Since experimental and theoretical investigations of their properties seem to indicate that there are no substantial differences between them or with respect to other superconducting cuprates, it is important to study the electronic structure of the full set of compounds in detail in order to carefully differentiate similarities and differences, and this will be the object of the present paper.

Attempts to rationalize the electronic structure of HTSC parent compounds and other transition metal (TM) compounds by means of the local density approximation (LDA) of density functional theory (DFT)<sup>22-28</sup> as well as the generalized gradient correction (GGA) to the exchange-correlation functionals<sup>22,29-31</sup> have been unsuccessful because they predict a too small band gap, indicating either a metallic or, in the most favorable cases, a semiconducting behavior; in some cases an inverted relative stability of the magnetic phases with respect to the experiment is also observed.<sup>22,28</sup> *Ad hoc* corrections for the self-interaction error (SIC) inherent to the local exchange functional have been proposed to remedy this LDA (and GGA) deficiency, such as LDA+SIC (Ref. 32) or LDA+U.<sup>33</sup> However, the use of these approaches has been rather limited. An interesting alternative approach to correct the self-interaction error of LDA consists in making use of hybrid functionals, such as B3LYP.<sup>34-36</sup> However, in spite of its overall balanced description of most of the relevant properties of the studied solids,<sup>37-41</sup> the B3LYP functional shows some limitations in describing magnetic coupling interactions (usually overestimates antiferromagnetic interactions by a factor 2 to 3) and is semiempirical in nature.

An alternative strategy is to use the *ab initio* unrestricted HF periodic approach.<sup>42-45</sup> This approach has previously been applied to several large gap TM oxides (Refs. 46-52) and fluorides (Refs. 53-60) including simple and complex 3D, 2D or (quasi)1D magnetic systems with different kinds of ions in several structures, bearing different spin moments, symmetric or strongly Jahn-Teller distorted. A qualitatively correct description of the insulating ground state and properties of the systems is attained: the optimized structural parameters and properties such as the formation energy, elastic, and magnetic coupling constants are in reasonable agreement with the experimental values.

Recently, embedded cluster model calculations of magnetic exchange in HTSC parent compounds and other TM compounds have been reported by Illas and collaborators<sup>61-66</sup> by using UHF and highly sophisticated configuration interaction (CI) schemes to account for the correlation effects on the relevant electronic states defining  $J_1$ . Small cluster models have been used which are, however, large enough for a careful determination of the first neighbor superexchange constants that are in good agreement with available experimental data.<sup>65-67</sup> From these studies it turns

out that magnetic coupling appears to be a rather local property and that UHF, while systematically underestimating the  $J$  value, is, however, able to reproduce trends along a family of compounds. The cluster model approach is obviously inappropriate to describe other important properties of solids which are long ranged, as for  $J_2$  and  $J_c$  in the present case, or originated by the periodicity of the system. These periodic<sup>46-60</sup> and cluster model<sup>51,52,59-66</sup> calculations on TM compounds indicate that UHF is able to provide a qualitatively correct description of the electronic structure of TM compounds and of the relative values of the magnetic coupling constants along a family or between magnetic interactions within the same compound.

The *ab initio* UHF periodic approach,<sup>42,43</sup> as implemented in the CRYSTAL98 code,<sup>44,45</sup> is the method chosen in the present work to study the crystal and electronic structures of the  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  (Refs. 8,9),  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$  (Refs. 10-13),  $\text{Sr}_2\text{CuO}_2\text{F}_2$  (Refs. 15-17), and  $\text{Ca}_2\text{CuO}_2\text{F}_2$  (Ref. 18), family of superconductor parent compounds in their common  $T$  ( $\text{La}_2\text{CuO}_4$ ) and  $T'$  ( $\text{Nd}_2\text{CuO}_4$ ) crystal varieties.

Previous theoretical approaches to some of the oxyhalide compounds considered in this work are based either on LDA or UHF band structure calculations as well as on the embedded cluster model approach. The early LDA approaches of Mattheiss,<sup>23,24</sup> stressed the importance of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  and  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$  oxyhalides as candidates for high- $T_c$  superconductivity. Three members of this family have been studied by Novikov *et al.*<sup>27</sup> at the LDA level; Wu and Zheng<sup>70</sup> explored the performance of LDA+U on  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ . The periodic UHF approach has been applied by Mackrodt, Gotsis, and Allan<sup>71</sup> to  $\text{Sr}_2\text{CuO}_2\text{F}_2$  and Su *et al.*<sup>50</sup> extended this approach to  $\text{La}_2\text{CuO}_4$ . Finally, the work of Illas and co-workers<sup>66,68</sup> focused on several monolayered cuprates including  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ ,  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ , and  $\text{Sr}_2\text{CuO}_2\text{F}_2$ . These authors found an important linear correlation between  $T_c$  and  $J/t$  for a wide series of monolayered cuprate materials,<sup>68</sup> that stresses the adequacy of the  $t$ - $J$  model and, hence, a pairing mechanism based on magnetic interactions. The values of  $J_1$  provided in their works<sup>66,68</sup> will be used as a reliable reference for the present calculations.

The present work is organized as follows. After the Introduction, the structures and relevant properties of the materials are described in Sec. II. The computational details are described in Sec. III. In Sec. IV, two subsections present the results: the crystal structures are discussed on the basis of the optimized crystal parameters and the electronic structure of the experimental phases is analyzed by means of the projected density of states and the spin and density maps (Sec. IV A). Magnetic interactions, calculated by means of the supercell approach, are discussed in Sec. IV B. Our conclusions are presented in Sec. V.

## II. CRYSTAL STRUCTURES AND PROPERTIES

The crystal structure of most of the monolayered HTSC's are related to the  $T$  and  $T'$  structures of  $\text{La}_2\text{CuO}_4$  (close to the prototypical layered perovskite  $\text{K}_2\text{NiF}_4$ ) and of  $\text{Nd}_2\text{CuO}_4$ , respectively. Most of these systems have been investigated at length during the late 1970's and 1980's in

their pure phase.<sup>9,13,14,18</sup> However, the discovery of the superconducting oxyhalides was made in the middle 1990's, since their synthesis needs special procedures (usually including high pressure) to permit the formation of metastable phases under ambient conditions and to control the dopant concentrations in an efficient way.<sup>10,11,15-17</sup> These new high pressure/high temperature synthetic methods opened the way to sintetize other important cuprate superconductor systems such as the infinite layered compound (Sr,Ca)CuO<sub>2</sub> (Refs. 72-74) or the ladder compounds.<sup>75,76</sup>

The family of the oxyhalide compounds with formula  $A_2\text{CuO}_2\text{X}_2$  with  $A = \text{Ca, Sr}$  and  $X = \text{F, Cl}$  are simple layered cuprates that exhibit the  $T$  and  $T'$  structures.  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$  and  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  show the simplest tetragonal  $T$  structure.<sup>8,10-12</sup> Closely related to the  $T$  structure is that of the  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  superconductors, showing an orthorhombic distorted structure.<sup>15,16</sup> The stoichiometric compound  $\text{Sr}_2\text{CuO}_2\text{F}_2$  (Ref. 17) and its Ca homologue (pure and with F excess)<sup>18</sup> crystallize, however, in the  $T'$  structure. Hole-type superconductivity has been found in the excess-fluorine compound  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  (with  $T_c^{\text{max}} = 46$  K at  $\delta = 0.6$ )<sup>15,16</sup> and  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  (with  $T_c^{\text{max}} = 26$  K at  $x \sim 0.08$ )<sup>11,12</sup> materials, both with the  $T$  structure. Moreover, the closely related compound  $\text{Sr}_{1.4}\text{Ba}_{0.6}\text{CuO}_2\text{F}_{2+\delta}$  is a  $p$ -type superconductor with  $T_c = 64$  K, one of the highest known critical temperatures for a monolayered HTSC with  $T$  structure.<sup>21</sup> In clear contrast,  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  also crystallizes with the  $T$  structure but has not been found to become superconductor, probably due to the large stability of the stoichiometric compound which is very difficult to dope, especially by cation substitution.<sup>8</sup>  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$  and the stoichiometric phase of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  crystallize in the  $T'$  structure; the former seems not to be superconducting for the available anion doping concentrations.<sup>18</sup> However, the effect of cation substitution on these oxyhalide cuprate systems has not been studied in extent, except for the  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  superconductors, and several experimental and theoretical studies on their properties and electronic structures indicate that these systems can develop a superconducting phase since there are no substantial differences between them and other cuprate superconductors.

$\text{Sr}_2\text{CuO}_2\text{Cl}_2$  is one of the most studied monolayered cuprates and usually is considered as a prototypical system representative of superconductor cuprate parent compounds.  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  has a charge transfer gap in the 1.4-1.9 eV range,<sup>77-79</sup> shows an antiferromagnetic order ( $T_N = 257$  K)<sup>80</sup> of the spin moments on the  $\text{Cu}^{2+}$  ions, each center bearing a magnetic moment of  $0.34\mu_B$ . The magnetic cell is twice the conventional one with the magnetic moments lying in the  $[1\ 1\ 0]$  direction on the (conventional)  $ab$  planes.<sup>81</sup> The magnetic order corresponds to a quasi-2D Heisenberg system with in-plane  $J_1 = 125 \pm 6$  meV (Refs. 78,80) and a much smaller interplane interaction.<sup>81</sup> It has been pointed out that in layered cuprates a next-nearest-neighbor magnetic coupling  $J_2$  exists and induces a magnetic frustration on the antiferromagnetic ground state of the planes, that can be important to the hole dynamics and the thermodynamic and spectroscopic properties of the pure and doped

materials.<sup>82-85</sup> The relative magnitude of these interactions ( $J_2/J_1$ ) is expected to be in the 0.08-0.2 range.<sup>82-88</sup>  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$  has been studied to a much less extent. It has been found to be a charge-transfer antiferromagnetic insulator ( $T_N \sim 250$  K)<sup>90,91</sup> with an electronic structure similar to  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  (Refs. 11,27,89). In the case of oxyfluorides, there are only few experimental studies, mainly addressed to structural and synthetic aspects.<sup>15-20</sup> However, the close similarity between the structures and the nature of the ions of this family of compounds is usually invoqued as an argument to suppose that the electronic structures and, hence, electronic and magnetic properties of the oxyfluoride systems are similar to those of the most studied oxychlorides.

### III. COMPUTATIONAL DETAILS

The calculations presented in this article have been performed by using the periodic HF approximation<sup>42,43</sup> in its unrestricted or spin polarized version<sup>44</sup> (in order to account for the open shell character of the systems), as implemented in the CRYSTAL98 code.<sup>45</sup> The crystalline orbitals are constructed as linear combinations of Bloch functions built from atomic orbitals (AO's) optimized for the crystal environment. The AO's are contracted real solid spherical harmonic Gaussian type functions (GTF's).

Extended all-electron basis sets have been used to describe  $\text{Cu}^{2+}$ ,  $\text{O}^{2-}$ , and  $\text{F}^-$  in the ionic environment. They can be indicated as 8-6-411-(41  $d$ )G (two  $d$  shells) for Cu, 7-311G for O and F, and contain 27 (Cu) and 13 (O and F) AO's, respectively. For  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Cl}^-$ , Hay and Wadt core pseudopotentials have been used to represent inner electrons of the ions [ $1s^22s^22p^6$  for  $\text{Cl}^-$  (Ref. 92) and  $\text{Ca}^{2+}$  and  $1s^22s^22p^63s^23p^63d^{10}$  for  $\text{Sr}^{2+}$  (Ref. 93)] and basis sets with 31G, 311G, and 31-(3  $d$ )G contraction schemes, respectively.<sup>94</sup> There are then, per unit cell, 93 AO's with 79 electrons for  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ , 95 AO's with 79 electrons for  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  and 105 AO's with 83 electrons for  $\text{Sr}_2\text{CuO}_2\text{F}_2$ .

The values adopted for the computational parameters that control the truncation of the Coulomb and exchange series<sup>43,45</sup> (7 7 7 and 14) ensure the high numerical accuracy required for the evaluation of energy differences of the order of  $10^{-7}$  Hartree/formula unit at fixed geometry, as is the case in the present study. A shrinking factor 4 has been used to define the reciprocal net in all the structures, corresponding to diagonalizing the Fock matrix at 21 points belonging to the irreducible Brillouin zone. The total energy difference obtained by using larger sampling nets is smaller than  $10^{-6}$  Hartree/cell.

The optimization of the structures has been performed considering the simplest primitive cell (which is necessarily in a ferromagnetic state) for each system, as indicated in Tables I, II, and III. For the analysis of the electronic structure and the evaluation of magnetic coupling constants the experimental cell parameters have been used. Three different supercells have been considered for the determination of magnetic exchange constants: the first one is the conventional (ferromagnetic) cell, with seven atoms. The second and the third ones are double cells suitable to generate the relevant antiferromagnetic phases that permit us to calculate

TABLE I. Calculated cell parameters and distances (in Å) of  $A_2\text{CuO}_2\text{Cl}_2$  ( $A = \text{Ca}, \text{Sr}$ ) for the ferromagnetic phase (corresponding to the conventional cell). The space group is  $I4/mmm$ , with atoms at  $\text{Cu}:(0,0,0)$ ,  $\text{O}:(0,1/2,0)$ ,  $\text{Cl}:(0,0,z_{\text{Cl}})$ , and  $\text{A}:(0,0,z_{\text{A}})$ . The volume of the conventional cell (in terms of the primitive cell, in Å<sup>3</sup>) and the corresponding UHF energy per formula unit (in Hartree) are also reported.

	$\text{Ca}_2\text{CuO}_2\text{Cl}_2$		$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	
	periodic UHF	Exptl. <sup>a</sup>	periodic UHF	Exptl. <sup>b</sup>
$a=b$	4.021	3.869	4.109	3.972
$c$	15.001	15.050	15.570	15.613
$z_{\text{Cl}}$	0.1822	0.1830	0.1800	0.1831
$z_{\text{A}}$	0.3950	0.3958	0.3925	0.3926
$V$	$121.27 \times 2$	$112.64 \times 2$	$131.44 \times 2$	$123.16 \times 2$
$E^{\text{UHF}}$	-1890.889310	-1890.877419	-1878.817821	-1878.808749
$d_{\text{Cu-O}}$	2.011	1.935	2.055	1.986
$d_{\text{Cu-Cl}}$	2.733	2.754	2.803	2.859
$d_{\text{Cu-Cu}}$	4.021	3.869	4.109	3.972
$d_{\text{Cu-A}}$	3.250	3.153	3.353	3.271
$d_{\text{O-A}}$	2.554	2.490	2.650	2.599
$d_{\text{Cl-A}}$	3.070	2.982	3.117	3.047

<sup>a</sup>From Argyriou *et al.* (Ref. 10).

<sup>b</sup>From Miller *et al.* (Ref. 8).

the nearest ( $J_1$ ) and next-nearest ( $J_2$ ) neighbor magnetic coupling constants in the  $\text{CuO}_2$  planes and the interplane magnetic coupling constant ( $J_c$ ). The extraction of the in-plane and the interplane magnetic coupling constants from these supercells is described in the next section.

## IV. RESULTS AND DISCUSSION

### A. Crystal and electronic structure

The crystal structure has been optimized by using the experimentally observed space-group symmetry by energy

TABLE II. Calculated cell parameters and distances (in Å) for the  $T$  ( $\text{La}_2\text{CuO}_4$ ) and  $T'$  ( $\text{Nd}_2\text{CuO}_4$ ) type of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  as obtained from the periodic UHF approach using the cell with one magnetic center (corresponding to the FM phase). The space group for the  $T$  ( $\text{La}_2\text{CuO}_4$ ) type is  $Fmmm$  with irreducible positions  $\text{Cu}:(0,0,0)$ ,  $\text{O}:(1/4,1/4,0)$ ,  $\text{F}:(0,0,z_{\text{F}})$ , and  $\text{Sr}:(0,0,z_{\text{Sr}})$ . For the  $T'$  structure the space group is  $I4/mmm$  with irreducible positions  $\text{Cu}:(0,0,0)$ ,  $\text{O}:(0,1/2,0)$ ,  $\text{F}:(0,1/2,1/4)$ , and  $\text{Sr}:(0,0,z_{\text{Sr}})$ . The volume of the conventional cell (in terms of the primitive cell, in Å<sup>3</sup>) and the corresponding UHF energy per formula unit (in Hartree) are also given.

	$\text{Sr}_2\text{CuO}_2\text{F}_2$ ( $T$ type)		$\text{Sr}_2\text{CuO}_2\text{F}_2$ ( $T'$ type)	
	periodic UHF	Exptl. <sup>a</sup>	periodic UHF	Exptl. <sup>b</sup>
$a$	5.613	5.394	4.059	3.967
$b$	5.613	5.513	4.059	3.967
$c$	13.330	13.468	12.820	12.816
$z_{\text{F}}$	0.1865	0.1802	0.25 (fixed)	0.25 (fixed)
$z_{\text{Sr}}$	0.3757	0.3680	0.3687	0.3650
$V$	$104.99 \times 4$	$100.12 \times 4$	$105.61 \times 2$	$100.84 \times 2$
$E^{\text{UHF}}$	-2048.270707	-2048.257014	-2048.261535	-2048.255743
$d_{\text{Cu-O}}$	1.984	1.928	2.023	1.984
$d_{\text{Cu-F}}$	2.486	2.427	3.794 (not apical)	3.768(not apical)
$d_{\text{Cu-Cu}}$	3.969	3.856	4.059	3.967
$d_{\text{Cu-Sr}}$	3.259	$3.230^4$ ( $3.280^4$ )	3.327	3.296
$d_{\text{O-Sr}}$	2.585	2.623	2.637	2.632
$d_{\text{F-Sr}}$	$2.522^1$ ( $2.926^4$ )	$2.529^1$ ( $2.774^2, 2.832^2$ )	2.537	2.471

<sup>a</sup>Derived from the work of Al-Mamouri *et al.* (Refs. 15,16).

<sup>b</sup>From Kissick *et al.* (Ref. 17).

TABLE III. Calculated cell parameters and distances (in Å) for the fictitious  $T$  ( $\text{La}_2\text{CuO}_4$ ) and the experimentally observed  $T'$  ( $\text{Nd}_2\text{CuO}_4$ ) types of  $\text{Ca}_2\text{CuO}_2\text{F}_2$  (simple cell data corresponding to the FM phase). The space group is  $Fm\bar{m}m$  ( $T$ ) with irreducible positions Cu:(0,0,0), O:(1/4,1/4,0), F:(0,0, $z_F$ ), and Ca:(0,0, $z_{Ca}$ ). For the  $T'$  structure the space group is  $I4/m\bar{m}m$  with irreducible positions Cu:(0,0,0), O:(0,1/2,0), F:(0,1/2,1/4) and Ca:(0,0, $z_{Ca}$ ). The volume of the conventional cell (in terms of the primitive one, in Å<sup>3</sup>) and the corresponding UHF energy per formula unit (in Hartree) are also reported.

	$\text{Ca}_2\text{CuO}_2\text{F}_2$ ( $T$ type)		$\text{Ca}_2\text{CuO}_2\text{F}_2$ ( $T'$ type)	
	periodic UHF		periodic UHF	Exptl. <sup>a</sup>
$a$	5.551(4)		3.955	3.850
$b$	5.551(0)		3.955	3.850
$c$	12.627		11.926	11.842
$z_F$	0.1927		0.25 (fixed)	0.25 (fixed)
$z_{Ca}$	0.3781		0.3683	0.3614
$V$	$97.27 \times 4$		$93.27 \times 2$	$87.76 \times 2$
$E^{\text{UHF}}$	-2060.368617		-2060.379152	-2060.369116
$d_{\text{Cu-O}}$	1.963		1.978	1.925
$d_{\text{Cu-F}}$	2.434		3.205 (not apical)	3.531(not apical)
$d_{\text{Cu-Cu}}$	3.926		3.956	3.850
$d_{\text{Cu-Ca}}$	3.174		3.208	3.179
$d_{\text{O-Ca}}$	2.495		2.526	2.530
$d_{\text{F-Ca}}$	2.340 <sup>1</sup> (2.916 <sup>4</sup> )		2.429	2.334

<sup>a</sup>From Al-Mamouri *et al.* (Ref. 18).

minimization of the ferromagnetic state. For  $\text{Sr}_2\text{CuO}_2\text{F}_2$  and  $\text{Ca}_2\text{CuO}_2\text{F}_2$  the  $T'$  ( $\text{Nd}_2\text{CuO}_4$ ) structure and the  $T$  (orthorhombic) structure have been optimized in order to compare the stability of the two phases, because, as pointed out in the previous section, stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$  and  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  compounds crystallize in different structures, but the  $\text{Ca}_2\text{CuO}_2\text{F}_{2+\delta}$  analogs only exist in the  $T'$  structure. The experimental and optimized geometries are given in Tables I, II, and III.

An interesting feature is that, when the  $Fm\bar{m}m$  orthorhombic structure of  $\text{Ca}_2\text{CuO}_2\text{F}_2$  and  $\text{Sr}_2\text{CuO}_2\text{F}_2$  is optimized, it collapses in the more symmetric  $I4/m\bar{m}m$  tetragonal structure. For  $\text{Sr}_2\text{CuO}_2\text{F}_2$  the optimized  $T$  phase is 24.08 kJ/mol more stable than the  $T'$  phase, whereas for  $\text{Ca}_2\text{CuO}_2\text{F}_2$  the optimized fictitious  $T$  phase is 27.66 kJ/mol

less stable than the  $T'$  phase. The structural stability of  $\text{Ca}_2\text{CuO}_2\text{F}_2$  is in agreement with experimental findings since only the  $T'$  phase is observed for the pure and excess fluorine compounds.<sup>18</sup> However, for stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$  the  $T'$  structure is less stable than  $T$ . Almost the same relative stability is obtained when correlation effects are included by means of the B3LYP hybrid functional for these structures. Hence, a point of disagreement remains for  $\text{Sr}_2\text{CuO}_2\text{F}_2$ . The cell volumes of the optimized structures is overestimated by  $\sim 6\%$  (slightly larger for the oxychlorides than for the oxyfluorides). In general, the Cu-O bond distances are overestimated by 3–4% whereas for apical Cu-X bond distances are underestimated by 1–2%. The overestimation of the distances and, hence, of the cell volumes is in line with that found in previous HF calculations for other TM compounds, and is a consequence of the so-called correlation error, due to the replacement of the electron-electron instantaneous interaction by a mean interaction.

The investigated compounds are described as very ionic materials; the Mulliken population analysis provides net charges (see Table IV) very close to the formal ionic ones. The strong ionic character is confirmed by bond populations, which are very small for the Cu-O bond and even smaller for other bonds. This points to a slightly larger covalent character on the  $\text{CuO}_2$  planes with respect to the bonds in the charge reservoir sheets or between those structural units of the crystal. The Mulliken analysis data are very similar for the ferromagnetic (FM) and AFM solutions, apart from the obvious spin inversion in the AFM case. It is also remarkable the nature of the magnetic moments in both phases which is almost independent of the magnetic solution. The spin density is localized on the  $\text{Cu}^{2+}$  ions ( $d^9$  open shell configuration) with very small spin densities on the other ions, due to a small spin polarization. The nature of the open shell bearing the spin density is almost pure  $d_{x^2-y^2}$ . The total and the spin density maps projected on the  $ab$  and  $ac$  planes are shown in Figs. 1 and 2. The total electron density maps show that, whereas the morphology of the density on the  $\text{CuO}_2$  planes are almost identical for the  $T$  and the  $T'$  structures, the morphology of the charge reservoir planes and the contact zone between these and the  $\text{CuO}_2$  sheets largely depends on the type of structure and less on the nature of their constituent ions. The  $d_{x^2-y^2}$  nature of the open shells on Cu ions is evident from the spin density maps. The small polarization on the nonmagnetic planes explains the small coupling be-

TABLE IV. Calculated net charge ( $q$ ) and total unpaired spin density ( $\sigma$ ) of the relevant ions ( $A = \text{Ca, Sr}$  and  $X = \text{F, Cl}$  depending on the compound) as resulting from a Mulliken analysis and indirect band gap ( $\Delta$ , in eV). The values for the FM and AFM phases are almost identical unless indicated.

compound	charge				spin				$\Delta$	
	$q_{\text{Cu}}$	$q_{\text{O}}$	$q_X$	$q_A$	$\sigma_{\text{Cu}}^{\text{FM}}$	$\sigma_{\text{O}}^{\text{FM}}$	$\sigma_{\text{Cu}}^{\text{AFM}}$	$\sigma_{\text{O}}^{\text{AFM}}$	$\Delta_{\text{FM}}$	$\Delta_{\text{AFM}}$
$\text{Ca}_2\text{CuO}_2\text{Cl}_2$	1.89	-1.94	-0.92	1.92	0.92	0.04	0.91	0.00	17.0	16.8
$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	1.83	-1.84	-0.97	1.89	0.93	0.04	0.91	0.00	16.7	15.9
$\text{Sr}_2\text{CuO}_2\text{F}_2$ ( $T$ )	1.90	-1.84	-1.02	1.91	0.92	0.04	0.91	0.00	12.1	13.0
$\text{Sr}_2\text{CuO}_2\text{F}_2$ ( $T'$ )	1.89	-1.88	-0.97	1.91	0.92	0.04	0.91	0.00	14.8	15.8
$\text{Ca}_2\text{CuO}_2\text{F}_2$ ( $T'$ )	1.89	-1.92	-1.00	1.98	0.91	0.05	0.90	0.00	13.6	14.7

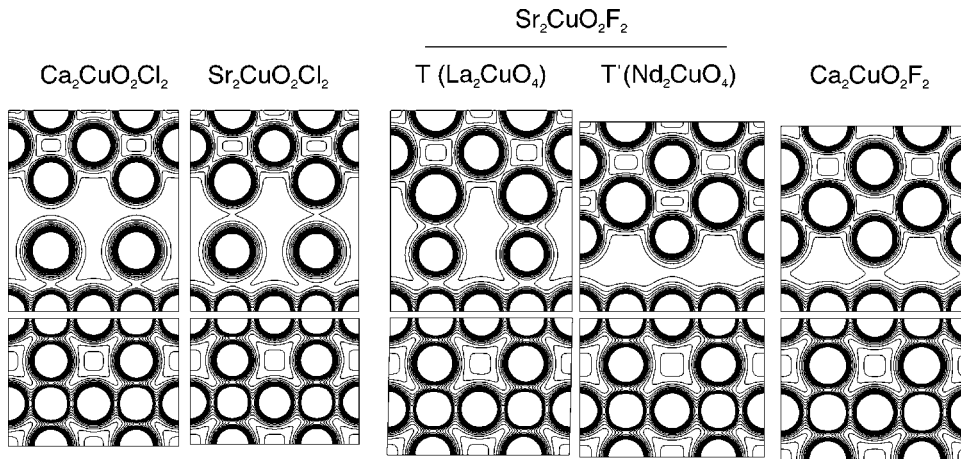


FIG. 1. Total electron density maps in a (100) plane (top) through the Cu, O, A (Ca or Sr) and X (F or Cl) ions, and (001) section through a  $\text{CuO}_2$  plane for the AFM magnetic phase. The separation between contiguous isodensity curves is  $0.01 |e|a_0^{-3}$  and the function is truncated in the atomic regions at  $0.15 |e|a_0^{-3}$ .

tween  $\text{CuO}_2$  planes along the  $c$  axis and confirms the strong 2D character of the crystal and magnetic structures of this kind of compounds.

The projected density of states (DOS) of the valence and conduction bands for the AFM case of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  and  $T$  and  $T'$  structures of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  are given in Figs. 3, 4, 5. The DOS graphs for the Ca compounds are very similar to their Sr analogs and are not reported. This and other additional data are available upon request to the authors. In all cases the band gap is very large respect to available experimental value. HF tends to overestimate this quantity by a factor 2–3 in highly ionic fluorides; this overestimation can be larger in oxides due to the highly correlated nature of these compounds.<sup>41,47,49,50,53–58</sup> It can be explained by the fact that conduction bands (virtual orbitals) are obtained in the Coulomb and exchange field of the total number of electrons of the unit cell. Consequently, the virtual orbital energies are too high as compared to excitation energies since there are large final state effects that are not taken into account. This problem is clear for the restricted HF approximation where the Koopman's theorem applies.<sup>95</sup> For the unrestricted, or spin polarized, HF approach the situation is less clear because there is no direct mathematical relationship between the one-electron levels issued from a spin-polarized HF calculation and the excitation energies (see for example the recent review of Baerends and Gritsenko<sup>96</sup> about the

physical meaning of Kohn-Sham and Hartree-Fock eigenvalues). As a consequence, the energy and orbital composition of the occupied bands are useful for the interpretation of optical spectra where the starting state is the ground state, whereas the role of the corresponding virtual orbitals, in particular the orbital energies, is more questionable.

The general structure of the DOS for the oxychloride systems is similar, with a broad set of O states from the top of conduction bands down to 6 eV. The Cl  $3p$  states form also a broad band that starts  $\sim 0.5$  eV below the Fermi level and decay near 5 eV from the Fermi level. The Cu  $3d$  states are grouped in four sharp bands near  $-7.5$ ,  $-9.0$ ,  $-10.0$ , and  $-11.5$  energies and the Ca  $3p$  and Sr  $4p$  are well below the Fermi level ( $-22.0$  and  $-17.0$  eV, respectively). For the oxyfluoride systems, the O bands extend down to  $-5.0$  eV and are well separated from the F  $2p$  states, that concentrate in the region between  $-9.0$  and  $-6.0$  eV, in the same range where the Cu  $3d$  states appear ( $[-12.0, -6.0]$  eV). These Cu states are also grouped in sharp bands with a dispersion larger than in the oxychloride compounds. The studied oxyhalide compounds show a strong O  $2p$  character of the highest occupied states that gives a charge transfer nature to the insulating gap. The distribution of the states is qualitatively different in oxychlorides and oxyfluorides: in oxychlorides the anion bands are at the top of the occupied states and separated from the Cu states, whereas in oxyfluoride com-

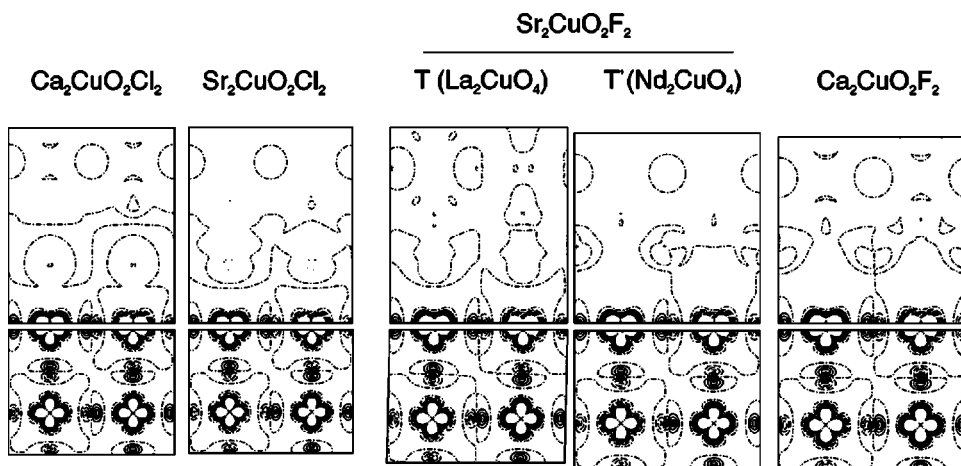


FIG. 2. Spin density maps in a (100) plane (top) through the Cu, O, A (Ca or Sr) and X (F or Cl) ions, and (001) section through a  $\text{CuO}_2$  plane for the AFM magnetic phase. The separation between contiguous isodensity curves is  $0.005 |e|a_0^{-3}$  and the most internal curves in the core regions correspond to  $\pm 0.05 |e|a_0^{-3}$ . Continuous, dashed and dot-dashed lines correspond to positive ( $\alpha$  density), negative ( $\beta$  density), and zero values of the function, respectively.

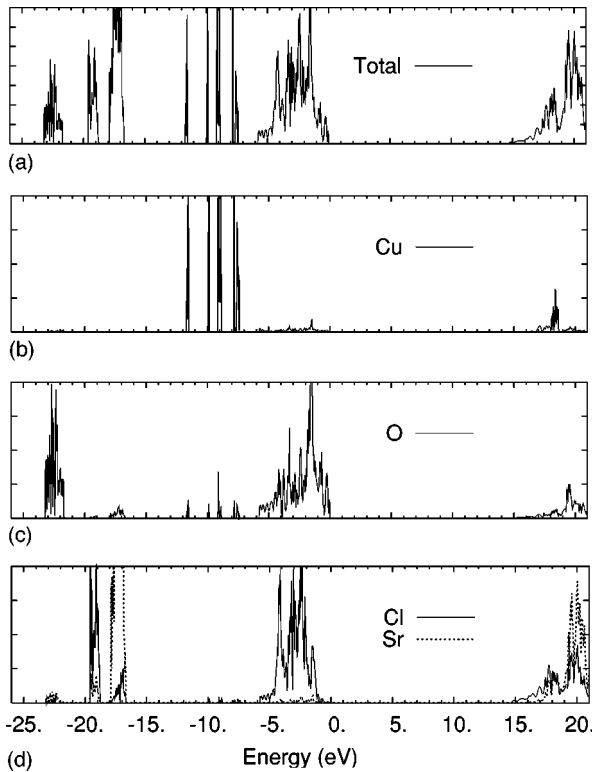


FIG. 3. Total and projected density of states of the antiferromagnetic phase of  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  at the experimental geometry [Miller *et al.* (Ref. 8)].

pounds the oxygen bands are at the top of the occupied states and separated from the Cu and F states, which largely overlap. However, differences between the compounds in each family are relatively small, and do not appear to be such to prevent the existence of a superconducting phase in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  or in  $\text{Ca}_2\text{CuO}_2\text{F}_2$ . Difficulties in the effective inclusion of the charge carriers by the available doping mechanisms are probably responsible for the lack of a superconducting transition in these systems.

The results reported here agree with the results of Mackrodt, Gotsis, and Allan<sup>71</sup> for  $\text{Sr}_2\text{CuO}_2\text{F}_2$  (the same theoretical approach and similar basis sets have been used); they are also in line with the results of Su *et al.*<sup>50</sup> However, there are fundamental differences with the available LDA results<sup>23,24,27</sup> where a metallic or semiconducting solution is obtained showing an (hypothetic) gap dominated by Cu  $d$  bands. Finally, the van Hove scenario analyzed by Novikov *et al.*<sup>27</sup> in these LDA calculations seems to be irrelevant for the microscopic mechanism<sup>2,7</sup> of superconductivity since the existence of an extended saddle-point-type singularity is neither a necessary nor a sufficient ingredient for superconductivity in cuprates.<sup>69</sup>

### B. Magnetic exchange interactions

The isotropic interaction between localized magnetic moments is commonly described by the phenomenological Heisenberg spin Hamiltonian

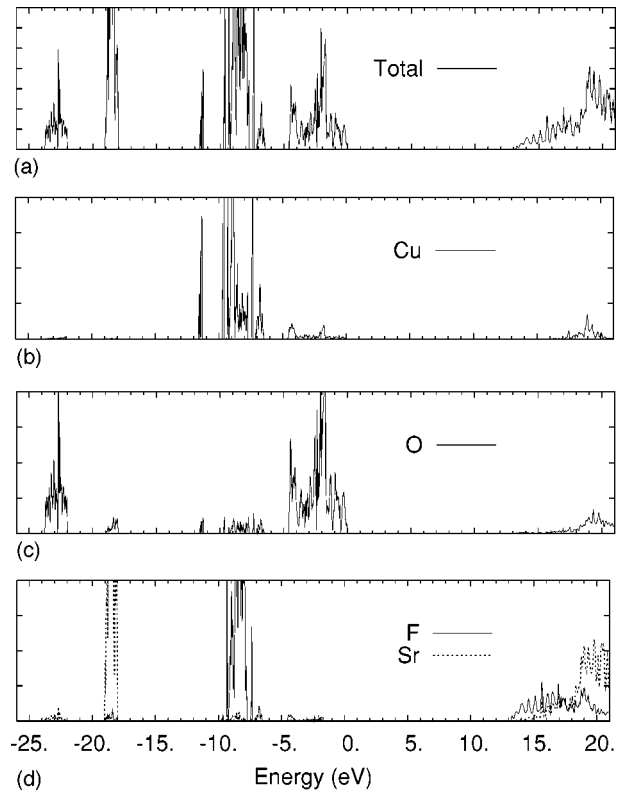


FIG. 4. Total and projected density of states of the antiferromagnetic phase of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  with  $T$  type ( $\text{La}_2\text{CuO}_4$ ) structure. Cell parameters have been derived from the structure determined by Al-Mamouri *et al.* (Refs. 15,16) for  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$ .

$$H^{\text{Heisenberg}} = - \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where  $\langle i,j \rangle$  indicates that interaction between near neighbor magnetic moments  $\mathbf{S}_i$  and  $\mathbf{S}_j$  are taken once and the  $\{J_{ij}\}$  constants give the magnitude and type of interaction between them. The  $\{J_{ij}\}$  set of parameters defining this magnetic Hamiltonians (its number and magnitude) results from the particular electronic structure and permits to describe the lower part of the excitation spectra. Their values are extracted by fitting to the experimental (or calculated) magnetic data.<sup>97</sup> In a useful simplification of the Heisenberg model, known as the the Ising model, only the  $S_{z,i}$  components of the  $\mathbf{S}_i$  magnetic moments are considered. The Ising model is introduced in order to solve the difficulties faced when solving the Heisenberg model. However, in some cases it is used to describe magnetic systems showing axial anisotropies in their magnetic interactions. Here, as the electronic monodeterminantal broken symmetry wave functions obtained at the UHF level are eigenfunctions of  $S_z$ , but not of  $S^2$ , the Ising model represents the natural reference spin hamiltonian for the mapping of the UHF energy differences in order to extract the magnetic coupling constants.<sup>61,62,98</sup> This procedure is equivalent to consider the mean-field approximation of the Heisenberg Hamiltonian [Eq. (1)] as recently discussed by Su *et al.*<sup>50</sup>

The superexchange mechanism was introduced by Anderson<sup>99</sup> to explain the antiferromagnetic coupling by

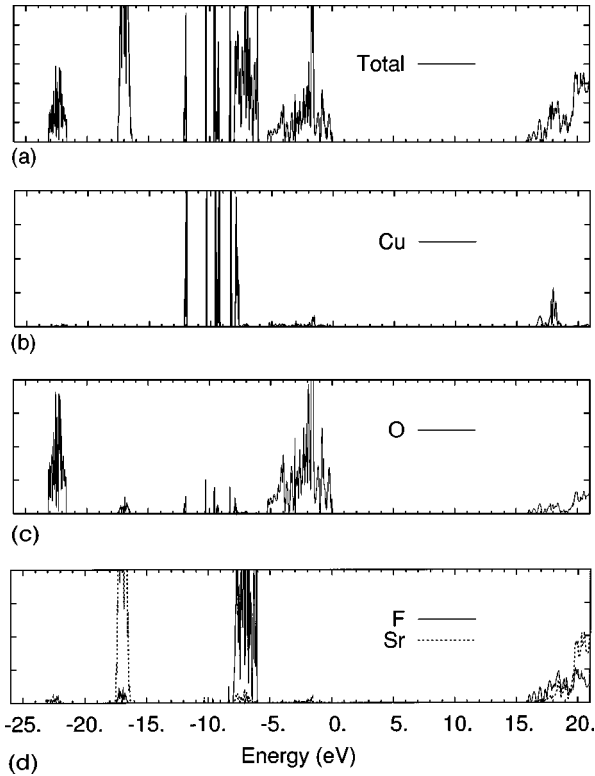


FIG. 5. Total and projected density of states of the antiferromagnetic phase of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  with  $T'$  type ( $\text{Nd}_2\text{CuO}_4$ ) structure. Cell parameters are those determined by Kissik *et al.* (Ref. 17) for stoichiometric  $\text{Sr}_2\text{CuO}_2\text{F}_2$ .

making use of the well-known Hubbard model Hamiltonian. In this approach, second-order perturbation theory leads to  $J \sim t^2/U$ , in a two-electron–two-center problem, which permits one to relate  $J$  and the parameters  $t$  (electron hopping integral) and  $U$  (on-site electron-electron repulsion) defining the Hubbard Hamiltonian. The UHF approach can, in principle, account for the superexchange mechanism but provides too small antiferromagnetic coupling constants—usually 20–30% of the experimental

value.<sup>62–65,100</sup> This behavior can be rationalized by the changes in  $J$  arising from changes in the effective parameters of the Hubbard Hamiltonian or, more precisely, in the  $t/U$  ratio, i.e., the delocalization/repulsion ratio, in a variable extent depending on the particular approach to describe the electronic structure, which may be dramatically exaggerated (as in LDA or GGA's) or underestimated (as in UHF) or, in other words, as due to the too small amount of electron-electron correlation taken into account this approach (hence to a too large  $U$  value).

Three different magnetic coupling constants have been calculated by means of the supercell approximation<sup>54–57</sup> to generate several magnetic orderings or magnetic phases. The experimental crystal structures given in Tables I, II, and III have been considered for all compounds. The simplest ferromagnetic ordering can be generated by using any of the supercells containing 2 or 4 Cu atoms per cell and the energy of those solutions is used as a coherence test between equivalent FM phases (differences are smaller than  $10^{-7}$  Hartree per formula unit). The first considered supercell permits to construct an antiferromagnetic phase, hereafter called AFM( $c$ ), consisting in ferromagnetic  $\text{CuO}_2$  planes alternating their spin along the  $c$  axis and is used to extract the interplane coupling constant. A second supercell has been used to construct the experimentally observed AFM phase formed by antiferromagnetic  $\text{CuO}_2$  planes in which each  $\alpha$  spin has four nearest neighbor  $\beta$  spins and four next nearest neighbor  $\alpha$  spins. The last supercell permits us to construct an antiferromagnetic phase, hereafter called AFM(2), which can be described as containing ferromagnetic [100] (or [010]) chains alternating their spins in the direction perpendicular to it. If one considers a magnetic spin Hamiltonian defined with three different dominant (or relevant) interactions, namely,  $J_1$ ,  $J_2$ , and  $J_c$ , the mapping between the energies (per formula unit) of the magnetic phases constructed and the Ising Hamiltonian permits us to establish the following relations:

$$E[\text{AFM}(c)] - E(\text{FM}) = 2J_c, \quad (2)$$

TABLE V. Magnetic coupling constants (in meV) at the experimental cell parameters. For  $\text{Sr}_2\text{CuO}_2\text{F}_2$ ,  $T$  and  $T'$  structures are considered.

compound	$J_1$	$J_2$	$J_c$	$J_1(\text{exptl.})^a$	$T_c^b$
$\text{Ca}_2\text{CuO}_2\text{Cl}_2$	-32.41	-0.673	$+0.62 \times 10^{-3}$	(-148)	28
$\text{Sr}_2\text{CuO}_2\text{Cl}_2$	-26.21	-0.507	$+0.66 \times 10^{-3}$	-125(-120)	N.S.
$\text{Sr}_2\text{CuO}_2\text{F}_2$ ( $T$ ) <sup>b</sup>	-32.09	-0.665	$+0.47 \times 10^{-3}$	(-140)	46
$\text{Sr}_2\text{CuO}_2\text{F}_2$ ( $T'$ )	-28.88	-0.792	$+0.55 \times 10^{-3}$		N.S.
$\text{Ca}_2\text{CuO}_2\text{F}_2$ ( $T'$ )	-35.74	-0.801	$+0.20 \times 10^{-3}$		N.S.

<sup>a</sup>An experimental value is available only for  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  (Ref. 80). The values in parenthesis are accurate predictions from highly correlated *ab initio* CI calculations on cluster models for the solids (from Refs. 66 and 68).

<sup>b</sup>Superconducting transition temperatures (in K) at optimal doping reported by Hiroi *et al.* (Refs. 11,12) for  $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$  ( $x \sim 0.08$ ) and by Al-Mamouri *et al.* (Refs. 15,16) for  $\text{Sr}_2\text{CuO}_2\text{F}_{2+\delta}$  ( $\delta = 0.6$ ).

<sup>c</sup>In the calculation of  $J_2$  a single average value has been assumed in equation 4 for simplicity. This is due to the fact that  $\text{CuO}_2$  planes show  $\text{CuO}$  plaquettes slightly distorted from the perfect square (88.75 instead of 90°) and two different next-nearest neighbor Cu-Cu distances appear (5.394 and 5.513 Å).



$$E(\text{AFM}) - E(\text{FM}) = J_1 + 2J_c, \quad (3)$$

and

$$E[\text{AFM}(2)] - E(\text{FM}) = \frac{1}{2}J_1 + J_2. \quad (4)$$

The resulting values derived for all the experimental structures are shown in Table V.

The most important magnetic interaction ( $J_1$ ) is underestimated with respect to the experimental value for  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , or the accurate values obtained by the cluster model approximation using highly correlated CI wave functions by Illas and co-workers.<sup>66,68</sup> However, the UHF values can provide useful *relative* values of the set of magnetic coupling constants defining the magnetic structure of the systems.<sup>41,54–56,59,60</sup> The UHF approach describes the magnetic order of these cuprates as 2D magnetic systems with almost independent antiferromagnetic planes (with  $J_c/J_1 \sim 10^{-3}$ ) showing a spin frustration due to the non-negligible next-nearest magnetic coupling (antiferromagnetic, with  $J_2/J_1 \sim 0.02$ ), slightly lower than the experimental estimates. These results are relevant since the thermodynamic properties of the pure systems and the dynamics of the charge carriers in the  $\text{CuO}_2$  planes can be largely affected by the existence of spin frustrations.<sup>82–87</sup> The comparison between the UHF values for  $J_1$  and those obtained by the cluster approach<sup>66,68</sup> can be used to derive an estimate of the experimental value of the magnetic coupling constant in the  $T'$  structures of the oxyfluorides: since the  $J_1^{\text{Cl}}/J_1^{\text{UHF}}$  ratio is 4.276, 4.578, and 4.358 for  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ ,  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ , and  $T'$  type of  $\text{Sr}_2\text{CuO}_2\text{F}_2$ , respectively, one can estimate  $J_1$  to be in the  $[-132, -123]$  meV range for the  $T'$  type of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  and  $[-164, -156]$  meV range for  $\text{Ca}_2\text{CuO}_2\text{F}_2$ . The unexpected large value for  $\text{Ca}_2\text{CuO}_2\text{F}_2$  is very interesting since it has been pointed out that the HTSC's with the largest  $T_c^{\text{max}}$  also show very strong antiferromagnetic coupling constants. Moreover, if a linear relation between  $T_c^{\text{max}}$  and the  $J/t$  relation is considered, and if the value of  $t$  is supposed to be close to 0.57 eV, the value derived for  $\text{Ca}_2\text{CuO}_2\text{Cl}_2$  using the same cluster approach, the expected value of  $T_c^{\text{max}}$  is in the  $[45, 55]$  K range which is close to the highest known critical temperature for a monolayered HTSC with  $\text{La}_2\text{CuO}_4$  structure.<sup>21</sup> In our opinion, the investigation of alternative doping processes of this material is an appealing research field since it should provide a new series of HTSC's and important tests of the present models of superconductivity.

## V. CONCLUSIONS

The structural, electronic, and magnetic properties of the  $\text{A}_2\text{CuO}_2\text{X}_2$  ( $A = \text{Ca}, \text{Sr}$  and  $X = \text{F}, \text{Cl}$ ) superconductor parent compounds have been investigated by using the *ab initio* periodic UHF method. The calculations correctly describe the systems as antiferromagnetic insulators with strong ionic character. The highest occupied bands have a strong oxygen  $2p$  character showing the charge transfer nature of the optical gap. The spin density is well localized on the  $\text{CuO}_2$  planes and arises from the  $d_{x^2-y^2}$  open shells of the ionic  $d^9$  configuration of the Cu atoms. The projected DOS are very similar for the oxyfluorides and the oxychlorides compounds, the only minor difference being in the position of the halide  $2p$  states. However, no significant differences between the electronic structures of the experimentally observed superconducting or non superconducting parent compounds have been found.

The UHF approach describes the magnetic order of these cuprates as 2D magnetic systems with almost independent antiferromagnetic planes showing a spin frustration due to a non-negligible value of  $J_2$ . The magnitude of  $J_1$  is underestimated with respect to available experimental or accurate theoretical values. In spite of these limitations, the periodic UHF method has been shown to correctly describe the magnetic order of ionic compounds and to give reasonably *ab initio* estimates for the magnetic coupling constants.

Finally, the close similarity between the electronic structure and properties of the oxyhalide cuprate compounds here investigated indicates that intrinsic limitations to develop a superconducting phase do not exist, and that kinetic limitations in the doping process can be at the origin of the fact that no superconducting transition has been observed in  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  and in the  $T'$  phase of  $\text{Sr}_2\text{CuO}_2\text{F}_2$  and  $\text{Ca}_2\text{CuO}_2\text{F}_2$ . Hence, the investigation of alternative doping processes of those materials is warmly suggested since it would provide a new series of HTSC's, and important validation of the present models of superconductivity.

## ACKNOWLEDGMENT

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