First principles calculations of solute-hole interactions in the high T_c oxyfluoride superconductor $Sr_2CuO_2F_2$

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Abstract

First principles periodic Hartree-Fock calculations are reported of the electronic and magnetic structures and hole states in the T (La_2CuO_4) phases of $Sr_2CuO_2F_2$, $Sr_2CuO_2F_{2.5}$ and $NaSrCuO_2F_2$. $Sr_2CuO_2F_2$ is predicted to be a highly ionic antiferromagnetic charge transfer insulator with Cu in a d^9 ($(d_{x^2-y^2})^1$) configuration. Holes are predicted to be highly localised spin polarons which destroy the AF ordering at concentrations of 0.5 per formula unit.

1. Introduction

Recent reports of high T_c superconductivity in $Sr_2CuO_2F_{2+\delta}$ below ~ 46 K by Al-Mamouri et al [1,2] have led to renewed interest in the electronic and magnetic structures of layered cuprates, on the basis of which fundamental explanations of their exotic properties are most likely to be found. As prepared, these materials are hyper-stoichiometric, with the superconducting regime in the range $0.2 < \delta < 0.6$ [1,2]. While it remains uncertain as to whether (fully-stoichiometric) $Sr_2CuO_2F_2$ adopts the T (La_2CuO_4) or T´ (Nd_2CuO_4) structure, the weight of evidence is that the superconducting material is T-phase. A previous FLMTO calculation [3] found ferromagnetic (T) $Sr_2CuO_2F_2$ to be conducting, with the assumption that antiferromagnetic ordering opens a gap at the Fermi level as the valence band is exactly half-filled at this energy. It was suggested that the maximum value of T_c occurs for $\delta \sim 0.38$ in the F excess system on the basis of a strong Van Hove singularity ~ 0.25 eV below ε_F. More recently, atomistic lattice simulations [4] predicted exclusive *axial* site occupancy by F in $Sr_2CuO_2F_2$ and that excess F occupies the same interstitial position as does excess O in $La_2CuO_{4+\delta}$, which is in agreement with the XES and PES data [2]. These simulations also predicted the solution energy of Na_2O in $Sr_2CuO_2F_2$ to be comparable to that for the incorporation of excess F, which suggested that materials within the phase $Na_xSr_{2-x}CuO_2F_2$ might exhibit high T_c behaviour. Here we continue this study of both F excess and Na-doped $Sr_2CuO_2F_2$ and report first principles Hartree-Fock calculations of the electronic and magnetic structures and hole states in T-phase $Sr_2CuO_2F_2$, $Sr_2CuO_2F_{2.5}$ and $NaSrCuO_2F_2$. Similar calculations have been used recently to give an accurate description of these same features for MnO and NiO [5-8].

2. Theoretical procedures

The all-electron first principles LCAO Hartree-Fock method for periodic systems and its computational implementation in the CRYSTAL 95 computer code [9] have been described in detail previously [10]. The calculations reported here use extended Gaussian basis sets and are based on the spin unrestricted (UHF) procedure of Pople and Nesbet [11] to describe open-shell electronic configurations. The computational procedures, tolerance parameters and numerical accuracies are identical to those used

for MnO and NiO [5-8], while details of the localised crystal orbitals will be reported separately [12]. Our treatment of the hole state is based on periodic super-cells which our computational resources have restricted to compositions of $Sr_4Cu_2O_4F_4$, ie one hole per two molecular units, which is approximately twice the concentration in the superconducting material. As before [7,8], a renormalisation of the (infinite) inter-cell Coulombic interaction in the case of the free hole is effected by adding a uniform background charge of opposite sign and equal magnitude to the crystal potential. This has no effect on the charge distribution or densities of states, other than a rigid shift in energy of the single particle spectrum.

3. Results

The UHF structure of $Sr_2CuO_2F_2$ obtained by direct energy minimisation is found to be similar to that proposed by Novikov et al [3] and that derived from atomistic simulations [13], details of which are given in Table 1. For all three structures the AF spin arrangement is lower than the FM by 0.049 eV/double unit cell, from which we derive a superexchange coupling constant, J_{se}, of -0.012 eV. An Ising model mean-field approximation of the type used previously for MnO and NiO [6] suggests that the Néel temperature of $Sr_2CuO_2F_2$ based on the UHF stabilisation energy of the AF arrangement will be substantially in excess of that of NiO (525 K). Table 2 lists the Mulliken populations of the three structures given in Table 1, from which it is clear that a UHF description of the T-phase of $Sr_2CuO_2F_2$ is that it is a highly ionic material in which Cu is in a d^9 ($(d_{x^2-y^2})^1$) configuration with a local moment of ~ 0.9 μ_B. From an analysis of the type used previously for MnO and NiO [6] we deduce a values of 0.9 – 1.3 eV for the Cu(d) *on-site* exchange energy. The densities of states (DOS) shown in Figure 1 confirm the strong ionicity and indicate that the valence band is essentially O(p) with the Cu(d) states confined to narrow bands below the F(p) band. The conduction band edge (CBE) (not shown in Figure 1) is predominantly Cu(d), so that $Sr_2CuO_2F_2$ is predicted to be a p $\rightarrow$ d charge transfer insulator with holes of essentially O(p) character in view of the negligible weight of Cu states at the valence band edge. The UHF valence band DOS is in stark contrast to the FLMTO DOS [3] where the Cu(d) states dominate the valence band up to the edge, which, in a rigid band approximation, suggests that holes will be predominantly Cu(d).

The removal of an electron from fully-symmetric $Sr_4Cu_2O_4F_4$ leads to an *insulating* state in which the unpaired electron/hole is delocalised over the all O sites, no matter what starting electronic configuration is chosen, with a further stabilisation of the AF ordering by ~ 0.5 eV. As reported previously for NiO [7] and MnO [8], the removal of this symmetry constraint allows the electronic configuration to relax to a non-degenerate state of *lower* energy in which the unpaired electron/hole is localised in a p_π orbital at a *single* O site. A Mulliken population analysis of this state suggests that over 90% of the hole is localised at this single O site with a local moment very close to 1 μ_B. It also indicates that Cu remains in a d^9 ($(d_{x^2-y^2})^1$) configuration with no loss of local moment. In common with MnO [8] the localised hole state favours the FM spin arrangement, here by ~ 0.8 eV with a *net* localisation energy of ~ 2.3 eV compared with the de-localised FM state. However, here the *high spin* state is favoured in which the spin of the unpaired $O(p_\pi)$ electron is *parallel* to the lattice spins. If we assume that the difference in energy between the FM and AF ordering can be written in terms of J_{se} and an *effective* $Cu(d_\sigma)$ - $O(p_\pi)$ spin-spin interaction energy, J_d, we deduce a value of - 0.86 eV for the latter. Since J_d is nearly two orders of magnitude greater than J_{se}, we predict the free hole in $Sr_2CuO_2F_2$ at a concentration of 0.5 per formula unit to show strong spin polaron character both below and above the Néel temperature.

Broken-symmetry calculations for $Sr_4Cu_2O_4F_5$, ie $Sr_2CuO_2F_{2.5}$, in which the interstitial position of the excess F, marked as X in Figure 1, is that calculated from atomistic simulations [4], once again lead to non-degenerate *insulating* states in which the un-paired electron/hole is localised in a p_π orbital at either the O_1 or O_2 site. The FM arrangement is lower in energy than the AF by 0.65 eV for both positions of the localised hole, with the O_1 site more stable of the two by 0.1 eV in the *unrelaxed* lattice. A Mulliken analysis confirms that the electronic configuration of the CuO_2 plane is identical to that containing a free hole with ~90% localisation of the hole and local moments of ~ 1 μ_B and ~ 0.9 μ_B at the hole and Cu sites respectively. Broken-symmetry calculations for $NaSrCuO_2F_2$ lead to very similar electronic configurations with the FM spin ordering now ~1.2 eV more stable than AF. As in the case of $Sr_2CuO_2F_{2.5}$ UHF calculations find $NaSrCuO_2F_2$ to be insulating.

4. Discussion

This paper is concerned primarily with the electronic structure and stability of hole states in $Sr_2CuO_2F_2$-based systems, which are p-type superconductors, in the light of recent reports which suggest that UHF calculations give an accurate description of the ground state electronic and magnetic properties of first-row transition metal oxides [5-8]. $Sr_4Cu_2O_4F_4^{(+)}$, ie $Sr_2CuO_2F_2$ with a free hole concentration of 0.5 per formula unit, is predicted to be *insulating* with the hole highly localised in a *single* $O(p_\pi)$ orbital. This destroys the antiferromagnetic order of the stoichiometric material as a result of strong $Cu(d_\sigma)$ - $O(p_\pi)$ spin-spin coupling which aligns the spins of the Cu nearest-neighbour to the hole site in a (high spin) ferromagnetic $Cu(\uparrow)$-$O(\uparrow)$-$Cu(\uparrow)$ configuration. From the energy difference between the FM and AF configurations we estimate this interaction (~ 0.9 eV), due to *non-local* exchange, to be comparable to the Cu(d) *on-site* exchange energy (~ 1 eV). This is in contrast to MnO [8] where holes are localised in $O(p_\sigma)$ orbitals leading to a low spin ferromagnetic configuration due to strong Pauli repulsion between $Mn(d_\sigma)$ and $O(p_\sigma)$ electrons with like spins. Here the spatial orthogonality of $Cu(d_\sigma)$ and $O(p_\pi)$ appears to obviate this repulsion. Since the electronic configuration of free holes in $Sr_2CuO_2F_2$ appears to be identical to that in $Sr_2CuO_2F_{2.5}$, which is close to the superconducting regime, it seems likely that magnetic (exchange) interactions of the type discussed here might be relevant to high T_c behaviour. Finally we note that the UHF description of $Sr_2CuO_2F_{2.5}$ as insulating, raises the interesting question as to whether the superconducting transition in systems close to this composition might be an insulator-to-superconductor transition.

5. Conclusions

The principal conclusions of this paper are (i) that the low temperature T-phase of $Sr_2CuO_2F_2$ is a highly ionic $p \rightarrow d$ charge transfer insulator in an antiferromagnetic spin arrangement of the CuO_2 planes with local moments of ~ 0.9 μ_B; (ii) that free holes are highly localised at O sites in p_π orbitals with local moments close to μ_B and strong spin polaron character; (iii) that antiferromagnetic order is destroyed by the presence of holes at a concentration of 0.5 per formula unit; (iv) that the electronic structure and stability of hole states in $Sr_2CuO_2F_2$ is due largely to the strong in-plane $Cu(d_\sigma)$-$O(p_\pi)$ coupling giving ferromagnetic $Cu(\uparrow)$-$O(\uparrow)$-$Cu(\uparrow)$ spin configurations;(v) that the

electronic configuration of CuO_2 planes in both $Sr_2CuO_2F_{2.5}$ and $NaSrCuO_2F_2$ is identical to that of planes containing the same concentration of free holes.

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Table 1. Predicted lattice structures of T-phase $Sr_2CuO_2F_2$. (Lattice constants are in Å, z_{Sr} and z_F in fractions of c_0)

Lattice constants	Hartree-Fock	Novikov et al [3]	Potentials Model [4]
a_0	3.97	3.86	3.89
c_0	13.33	13.47	13.57
z_{Sr}	0.12	0.13	0.11
z_F	0.19	0.18	0.18

Table 2. The total Mulliken charges, q_M (e), 3d population, n_{3d} and local spin moment at Cu, n_s (μ_B), of AF $Sr_2CuO_2F_2$ in the UHF structure compared with those of references 3 and 4.

Structure	q_M(Sr)	q_M(Cu)	q_M(O)	q_M(F)	n_{3d}	n_s
H-F	1.90	1.85	1.85	1.98	9.09	0.93
Ref [3]	1.90	1.83	1.83	1.99	9.11	0.92
Ref [4]	1.90	1.83	1.84	1.99	9.11	0.91

Table 3. Summary of energies (eV) of the FM and AF states of the T-phases of $Sr_2CuO_2F_2$, $Sr_2CuO_2F_{2.5}$ and $NaSrCuO_2F_2$, where $\Delta E = E_{FM} - E_{AF}$.

Structure	Energy
ΔE ($Sr_2CuO_2F_2$)	0.049
Super-exchange constant, J_{se}	- 0.012
AF $Sr_2CuO_2F_2$ - hole localisation energy	0.90
FM $Sr_2CuO_2F_2$ - hole localisation energy	2.27
ΔE ($Sr_2CuO_2F_2$) - localised hole	- 0.82
Cu(d_σ) - O(p_π) spin-spin coupling energy	- 0.86
ΔE ($Sr_2CuO_2F_{2.5}$) - O_1 hole site	- 0.65
$E(Sr_4Cu_2O_3O_1(h)F_4)$- $E(Sr_4Cu_2O_3O_2(h)F_2)$	- 0.10
ΔE ($NaSrCuO_2F_2$)	- 1.17

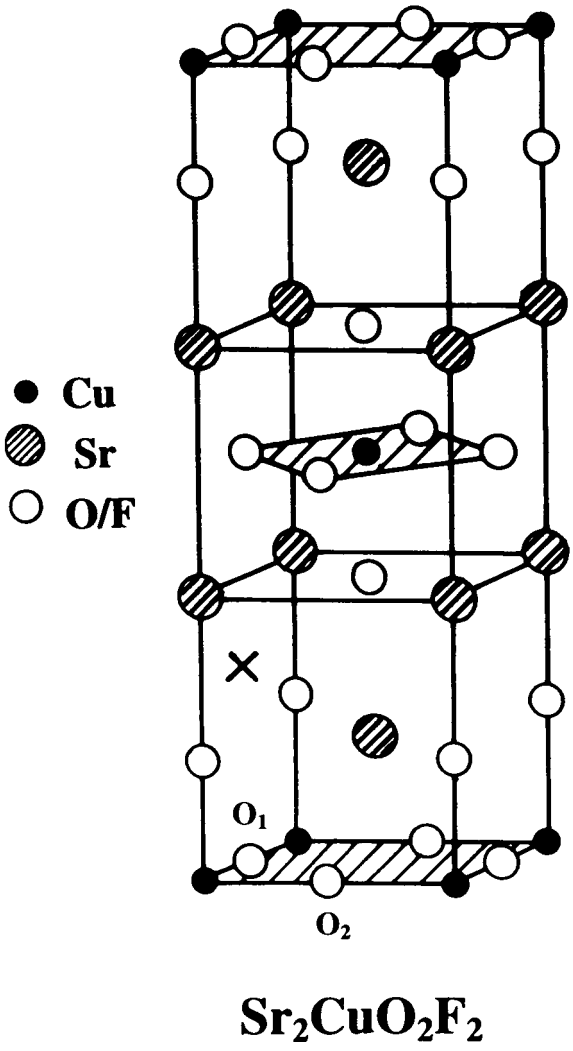

Figure 1. T-phase crystal structure of $Sr_2CuO_2F_2$. X marks the position of the interstitial in $Sr_2CuO_2F_{2.5}$

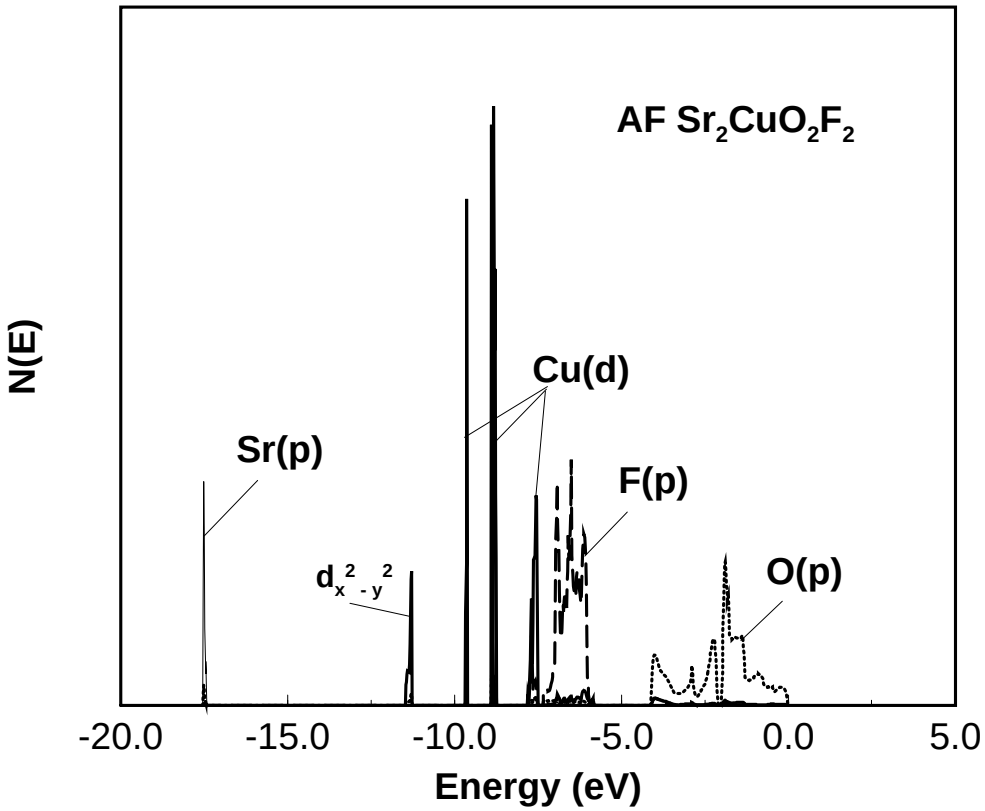

Figure 2. Valence band DOS of $Sr_2CuO_2F_2$