Atomistic simulation of $M_2CuO_2F_{2+\delta}$ (M = Ca,Sr)

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Atomistic simulations predict that fluorine ions occupy axial sites in $Sr_2CuO_2F_2$ and $Ca_2CuO_2F_2$ with minimal O/F disorder and that excess fluorine occupies the same interstitial site in $Sr_2CuO_2F_2$ as in $La_2CuO_{4+\delta}$; calculated solution energies of BaO in $Sr_2CuO_2F_2$ are consistent with the formation of $Sr_{1.4}Ba_{0.6}CuO_2F_{2+\delta}$, while the predicted energy and mode of solution of Na_2O in $Sr_2CuO_2F_2$ suggest $(Na/K)_xSr_{2-x}CuO_2F_2$ warrants investigation for possible high-T_c behaviour.

Since the historic discovery of high-T_c superconductivity in La_2CuO_4 by Bednorz and Müller,[1] there have been several important developments with regard to the type of system that exhibits this exotic behaviour. One of these developments is the recent synthesis of oxyfluorides of the type $M_2CuO_2F_{2+\delta}$ (M = Ca,Sr),[2,3] of which $Sr_2CuO_2F_{2+\delta}$ has been shown to be a p-type superconductor ($T_c \approx 46$ K), unlike $Ca_2CuO_2F_{2+\delta}$ which does not appear to share this property. Furthermore, the mixed alkaline-earth oxyfluoride, $Sr_{1.4}Ba_{0.6}CuO_2F_{2+\delta}$, is also a p-type superconductor with a T_c of 64 K.[4] Here, we address two key issues related to the superconductivity of these systems. They concern the location of fluorine in both the stoichiometric ($\delta = 0$) and non-stoichiometric materials, and cation doping. Our approach, which is based on atomistic lattice simulations,[5–7] follows that used previously to describe correctly the fluoridation of Nd_2CuO_4 and La_2CuO_4. Calculations based on a relatively simple ionic model[8,9] predicted that fluoridation of Nd_2CuO_4 leads to F^- substitution for O^{2-}, *i.e.* $F_o^{\bullet}$ in Kröger–Vink notation, and the formation of defect electrons, which are the precursors to the observed n-type superconductivity in this system.[10] These calculations[8] also indicated that, in marked contrast, the direct fluorination of La_2CuO_4 leads to the incorporation of interstitial fluoride (F_i') (*cf.* excess oxygen) and the formation of holes, which subsequently Bose condense to give a p-type superconductor, as reported.[11] Details of the modified ionic model employed and the theoretical methods used for these athermal simulations of perfect and defective lattices are available elsewhere,[8] as are full details of the interionic potentials.†

Whereas Sr_2CuO_3 contains CuO_2 chains rather than CuO_2 planes, $Sr_2CuO_2F_{2+\delta}$ has the La_2CuO_4 structure (Fig. 1). However, the exact location of oxygen and fluorine remain uncertain, for neither X-ray nor neutron diffraction can differentiate clearly between the two due to the similarity of their scattering factors. This is clearly an issue of considerable importance for theories of high-T_c behaviour, notably the putative integrity of CuO_2 planes in high-T_c materials, and a question well suited for study by atomistic simulation techniques.

Starting with the stoichiometric material, $Sr_2CuO_2F_2$ is predicted to adopt the La_2CuO_4 structure in preference to that of Nd_2CuO_4, with an energy difference of *ca.* 1.5 eV per formula unit between the two. The calculated lattice constants are 3.889 and 13.57Å for a_0 and c_0 which are within 0.8 and 0.7% of the experimental values of 3.857 and 13.47 Å respectively.[12] The energy difference per formula unit between the structure with both fluorines axial and that with two equatorial fluorines is *ca.* 1.1 eV, while the energy of the anti-site defect, $F_O^{\bullet}/O_F'$, in which a single oxygen and fluorine interchange, is calculated to be *ca.* 0.8 eV. Thus we predict fluorine to occupy the axial sites of the unit cell with very little structural disorder of the CuO_2 planes.

The lowest energy interstitial position for additional fluorine in $Sr_2CuO_2F_{2+\delta}$ is predicted to be (0,0.5, *ca.* 0.25) (see Fig. 1), in which the interstitial is eight-coordinate. This is the position occupied[13] by excess oxygen in $La_2NiO_{4+\delta}$, and also that predicted[8] for the super-stoichiometric oxygen in $La_2CuO_{4+\delta}$. In the fully relaxed structure the four nearest fluorines are displaced from their normal lattice sites away from the negatively charged interstitial, F_i', in agreement with experiment.[2] Neutron diffraction studies[14] of $La_2CuO_{4+\delta}$ suggest this is the favoured position for oxygen in this type of structure, although for La_2CuO_4 itself they also suggest a short interstitial/lattice O–O bond length, which is not reproduced by the calculations.

Incorporation of excess oxygen in La_2CuO_4 leads to the generation of holes in the CuO_2 planes resulting in p-type high-T_c behaviour. Lattice simulations suggest the same is true for excess fluorine in $Sr_2CuO_2F_2$ according to eqns. (1) and (2):

$$Sr_2CuO_2F_2 + (\delta/2)F_2 \rightarrow Sr_2CuO_2F_{2+\delta} \tag{1}$$

$$\tfrac{1}{2}F_2(g) \longrightarrow F_i' + h^{\bullet} \tag{2}$$

The calculated energy for this reaction is *ca.* −0.1 eV, which compares with a value of 0.7eV found previously[8] for oxygen incorporation in La_2CuO_4. The calculated energy for the alternative reaction [eqn. (3)], which would lead to n-type behaviour, is by contrast, very high at >1.5eV.

$$\tfrac{1}{2}F_2(g) + O_O^{x} \longrightarrow \tfrac{1}{2}O_2(g) + F_O^{\bullet} + e' \tag{3}$$

The mode of solution of dopant ions is of crucial importance in high-T_c materials due to the widespread extrinsic control of the charge carriers. In particular, the recent synthesis[4] of $Sr_{1.4}Ba_{0.6}CuO_2F_{2+\delta}$ indicates that $Sr_2CuO_2F_2$ can accommodate an appreciable fraction of Ba. Accordingly, we have calculated the solution energy of BaO, E_{Ba}, in $Sr_2CuO_2F_2$ according to eqn. (4).

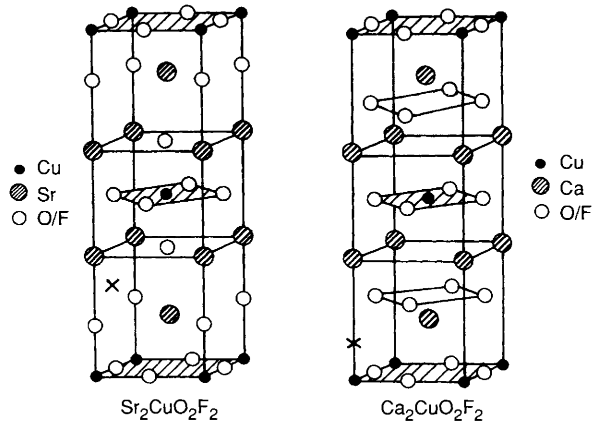

Fig. 1 The crystal structures of $Sr_2CuO_2F_2$ and $Ca_2CuO_2F_2$. The calculated positions for interstitial fluorine are marked with a cross.

$$\mathrm{BaO} + \mathrm{Sr}_{\mathrm{Sr}}^{\mathrm{X}} \longrightarrow \mathrm{Ba}_{\mathrm{Sr}} + \mathrm{Sr}_{\mathrm{Sr}}^{\mathrm{X}} + \mathrm{O}_{\mathrm{O}}^{\mathrm{X}} \qquad (4)$$

E_{Ba} is calculated to be −0.6 eV which, in the absence of a precise experimental value, is consistent with the observed solubility of BaO. Prompted by this result and by our previous calculations[5] of the defect structure of alkali-metal-doped La_2CuO_4, we have also calculated the solution energy of Na_2O, E_{Na}, according to eqn. (5).

$$\tfrac{1}{2}\,\mathrm{Na_2O} + \mathrm{Sr}_{\mathrm{Sr}}^{\mathrm{X}} + \tfrac{1}{4}\,\mathrm{O_2}\,(\mathrm{g}) \longrightarrow \mathrm{Na}_{\mathrm{Sr}}' + \mathrm{h}^{\bullet} + \mathrm{Sr}_{\mathrm{Sr}}^{\mathrm{X}} + \mathrm{O}_{\mathrm{O}}^{\mathrm{X}} \qquad (5)$$

The calculated value of E_{Na} is −0.1 eV. This is very close to that for the incorporation of excess fluorine in $Sr_2CuO_2F_2$, which suggests that, in the absence of second phase formation, the requisite concentration of holes for Bose condensation should be achievable. Solutions of Na_2O (and by inference K_2O) in $Sr_2CuO_2F_2$, therefore, would seem to be worth investigating for potential high-T_c behaviour.

Unlike $Sr_2CuO_2F_{2+\delta}$, the corresponding Ca compound, $Ca_2CuO_2F_{2+\delta}$, which has also been prepared recently,[3] adopts the Nd_2CuO_4 structure (Fig. 1). It does not exhibit superconducting behaviour, which is consistent with the known absence of hole, as opposed to electron, superconductivity in this type of structure. The calculated lattice constants of $Ca_2CuO_2F_2$ are 3.852 and 11.86 Å for a_0 and c_0 which are within 0.1 and 0.2% of the experimental values[3] of 3.850 and 11.84 Å, respectively, for $Ca_2CuO_2F_{2.1}$. In common with $Sr_2CuO_2F_{2+\delta}$, lattice simulations indicate a strong preference of F^- for the extraplanar (4d) sites, with O/F anti-site energies in excess of *ca.* 1.0 eV. In both systems, therefore, the disorder of the CuO_2 planes is predicted to be minimal. Despite the close agreement with the experimental (Nd_2CuO_4) structure, the lattice energy of the La_2CuO_4 structure is calculated to be lower by 0.5 eV per formula unit in the athermal limit. While this might suggest a possible failure of our model for $Ca_2CuO_2F_2$, we note first that our calculations refer to the stoichiometric system, and second that structural refinements[3] of $Ca_2CuO_2F_{2.1}$ have suggested the existence of regions with the La_2CuO_4 structure. This is entirely consistent with our calculated F^- interstitial position in $Ca_2CuO_2F_2$ which is exactly the axial site occupied by F^- in the La_2CuO_4 type of structure and also that occupied[15] by interstitial oxygen in $Nd_2CuO_{4+\delta}$. Furthermore, our conclusions as to the preferential location of F^- in the fluorine excess system is in complete agreement with the most recent suggestions[16] from X-ray emission and photoelectron spectra.

Finally, we comment that the differences in (superconducting) behaviour between $Sr_2CuO_2F_{2+\delta}$ and $Ca_2CuO_2F_{2+\delta}$ might reasonably be attributed to the different formation energies of defect electrons and holes in La_2CuO_4- and Nd_2CuO_4-type structures, as emphasised elsewhere.[9]

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Footnote

† Details of the potentials are available as supplementary data, or from the authors by E-mail (n.l.allan@bris.ac.uk)

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