Defect chemistry of the oxyfluoride $Sr_2CuO_2F_{2+\delta}$: relationship to high-T_c superconductivity

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Computer simulations of the oxyfluoride superconductor $Sr_2CuO_2F_{2+\delta}$ predict that fluorine incorporation at interstitial sites is the most favourable hole-doping mechanism in accord with experimental models.

The copper oxyhalides, $Sr_2CuO_2F_{2+\delta}$,[1] $(Ca,Na)_2CuO_2Cl_2$[2] and $(Sr,Ca)_3Cu_2O_{4+\delta}Cl_{2-y}$,[3] have opened up a new family of high-temperature superconductors with the halide ion replacing the apical oxygen in the crystal structures. These oxyhalides have generated considerable interest with important implications for our understanding of superconducting behaviour in the cuprate materials. It is well established that defect processes play a crucial role in determining the properties of superconducting compounds. In the case of the $Sr_2CuO_2F_{2+\delta}$ phase, which has an La_2CuO_4-type structure and a transition temperature (T_c) of 46 K, it is believed that the p-type superconductivity is induced by oxidation involving interstitial F ions.[1,4] In contrast, high T_c superconductivity in $(Sr,Ca)_3Cu_2O_{4+\delta}Cl_{2-y}$ is associated with oxygen substitution for chlorine.[3]

Calculations in this area are amenable to modern computer simulation techniques and are particularly useful in probing the nature of the reactions that are responsible for the formation of charge carriers. The purpose of this study is to use such techniques to investigate the defect chemistry of $Sr_2CuO_2F_{2+\delta}$ which is the first high-temperature superconductor in which fluorine plays a vital role. These simulation methods are now well tested tools for exploring solid-state properties on the atomic scale, and have been applied successfully to a range of superconductors[5,6] and complex oxides.[7] The significance of the present communication is that it offers an explanation based on calculated energetics as to why a particular 'hole-doping' mechanism is found in $Sr_2CuO_2F_{2+\delta}$.

The present account of these techniques (embodied in the CASCADE code[8]) will be brief since comprehensive reviews are given elsewhere.[9] The potentials describing the interatomic interactions are represented by ionic pair-wise potentials which include the long-range Coulomb term and an analytical function to model overlap repulsions and van der Waals forces. The shell model[10] provides a simple description of ionic polarisability and has proved to be effective in simulating the dielectric and lattice dynamical properties of ceramic oxides. An important feature of these calculations is the treatment of lattice relaxation about the point defect. The Mott–Littleton approach[9] is to partition the crystal lattice into two regions so that ions in an inner region surrounding the defect are relaxed explicitly, whereas the remainder of the crystal is treated by quasi-continuum methods.

As our starting configuration, $Sr_2CuO_2F_2$ adopted the idealized K_2NiF_4 structure[11] which allowed us to investigate the incorporation of fluorine into the parent ($\delta = 0$) compound. A similar approach has been used for recent band-structure calculations of $Sr_2CuO_2X_2$ (where X = F, Cl).[11] The short-range potential parameters assigned to each ion–ion interaction were derived by empirical fitting to the structural properties.[12] Prior to carrying out the defect calculations, energy minimization of the perfect lattice is performed to generate an equilibrium structure. The calculated and experimental lattice parameters are listed in Table 1 which reveals good agreement between simulated and observed structures. In addition, the lattice energy and relative permittivities for the perfect crystal have been calculated and are also reported in Table 1. Corresponding experimental data are currently unavailable and would be useful for further validation and refinement of the potential model.

Powder diffraction experiments[1] suggest that the excess fluorine (δ) occupy interstitial sites near the 'ideal' ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) position (Fig. 1), with significant displacement of neighbouring F ions. However, accurate refinement of these two site occupancies independently has been difficult. To investigate

Table 1 Calculated crystal properties of $Sr_2CuO_2F_2$

Property	$Sr_2CuO_2F_2$
Lattice parameters	
a/Å	3.873 (3.857)[a]
c/Å	13.485 (13.468)[a]
Lattice energy/eV	−101.37
Relative permittivities	
$<\varepsilon_0>$	18.4
$<\varepsilon_\infty>$	2.3

[a] Observed values[11] in parentheses.

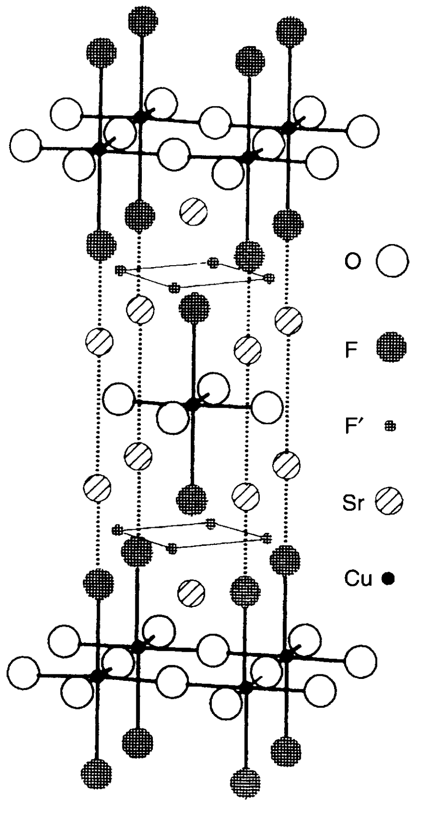

Fig. 1 Crystal structure of $Sr_2CuO_2F_{2+\delta}$ showing idealized apical (F) and interstitial (F′) sites (after ref. 1)

this problem, calculations were first performed on the isolated fluorine interstitial in the $Sr_2CuO_2F_2$ 'parent' compound. Following extensive search of the potential energy surface, the most favourable interstitial position is found to be (0.251 0.250 0.251) with four Sr^{2+} and four F^- nearest neighbours. This result is consistent with the ideal position in the crystal structure already postulated from diffraction studies.[1,13] Analysis of the local structure indicates significant outward displacements of the neighbouring apical F ions of up to 0.7 Å away from the interstitial; this local relaxation accords well with that reported by Al-Mamouri *et al.*[1] who find the apical F shifting by *ca.* 0.6 Å. It is worth noting that the calculated local structure is also consistent with that found for the oxygen interstitial defect in $La_2NiO_{4+\delta}$ (ref. 13), but slightly different from the model proposed for $La_2CuO_{4+\delta}$ that includes a short O···O separation.[14]

For $YBa_2Cu_3O_{6+\delta}$ and the mercury cuprates (*e.g.* $HgBa_2Ca_2Cu_3O_{8+\delta}$), oxygen incorporation is the hole-doping mechanism responsible for superconducting behaviour. Similarly, the itinerant holes in $Sr_2CuO_2F_{2+\delta}$ are believed to be generated by charge-compensation for excess fluorine. Simulations in this area can be effective in examining the nature of the oxidation–reduction reactions that create charge carriers. We have therefore considered the following reactions in $Sr_2CuO_2F_2$.

(*i*) Oxidation to form holes from fluorine incorporation as interstitial defects:

$$1/2\ F_{2(g)} = F_i' + h^{\cdot} \qquad (1)$$

where, in Kroger–Vink notation, F_i' is a fluorine interstitial and $h^{\cdot}$ is a hole.

(*ii*) Oxidation to form holes from oxygen incorporation as interstitial defects:

$$1/2\ O_{2(g)} = O_i'' + 2h^{\cdot} \qquad (2)$$

(*iii*) Oxidation to form holes from oxygen substitution of apical fluorine:

$$1/2\ O_{2(g)} + F_F^X = O_F' + 1/2\ F_{2(g)} + h^{\cdot} \qquad (3)$$

which is similar to the 'anion-doping' mechanism found in the oxychloride $(Sr,Ca)_3Cu_2O_{4+\delta}Cl_{2-y}$ ($T_c = 80$ K).[3]

(*iv*) Reduction to form electrons from fluorine substitution of oxygen:

$$1/2\ F_{2(g)} + O_O^X = F_O^{\cdot} + 1/2\ O_{2(g)} + e' \qquad (4)$$

This process seems unlikely as it would lead to n-type (super)conductivity which has not been observed in this system. Nevertheless, in view of the occurrence of n-type behaviour in related oxides, it is worth investigating.

Our studies have favoured copper holes over oxygen holes although we acknowledge that the question of whether such species have predominantly Cu(3d) or O(2p) character remains controversial. Nevertheless, our main concern here is to understand how hole species might form; for this task our simulation procedures have proved to be reliable. The merit of our approach is that it includes detailed estimates of lattice polarization and Coulomb energies which are difficult to make from other sources. The energies of these four reactions are collected in Table 2, and were derived using relevant defect and intra-atomic energy terms (also given in Table 2).

Table 2 Calculated energies for defect (redox) reactions in $Sr_2CuO_2F_2$[a]

Redox process	E/eV
Oxidation	
reaction (1)	−0.36
reaction (2)	0.77
reaction (3)	2.03
Reduction	
reaction (4)	4.59

[a] Atomic energy terms in eV: F_2 dissociation (1.64); O_2 dissociation (5.16); electron affinity of F (−3.40); first and second electron affinities of O (−1.47, 8.75); Cu hole (3.37); Cu electron (1.03).

Three points emerge from these results. First, the negative value for reaction (1), indicating a highly favourable process, agrees with observation as it is known that $Sr_2CuO_2F_{2+\delta}$ has a high solubility for excess fluorine.[1,14] Our results therefore confirm that this reaction, involving interstitial F, is responsible for the introduction of the holes necessary for p-type superconductivity. While no direct comparison can be made with measured energies, our calculated value is consistent with oxidation enthalpies of other cuprate materials.[5,6] Second, the high positive value for the reduction reaction (4) involving electron formation suggests that $Sr_2CuO_2F_{2+\delta}$ is resistant to n-type behaviour. In this respect, it is interesting to note the report of unsuccessful attempts to induce n-type behaviour in $Ca_2CuO_2F_{2+\delta}$ (ref. 15), which is structurally related to the n-type superconductor Nd_2CuO_4. Finally, it is evident that the oxidation reaction (3) with replacement of apical F^- ions by O^{2-} is energetically unfavourable, suggesting that this process is unlikely to be of any significance in this material.

In conclusion, our computer simulation study has highlighted the importance of defect reactions in $Sr_2CuO_2F_{2+\delta}$ that relate to high T_c behaviour. The calculated energies show that incorporation of interstitial F [eqn. (1)] is the most favourable (and exothermic) reaction, thereby giving an explanation, based on quantitative calculations as opposed to qualitative arguments, as to why this process is responsible for the generation of holes necessary for superconductivity in this material.

The project was supported by funds from the Chemistry Department at Surrey University. We are grateful to Sakib Khan and Mark Read for their assistance and to the University of London Computer Centre (ULCC) for the provision of supercomputer resources.

References

1 M. Al-Mamouri, P. P. Edwards, C. Greaves and M. Slaski, *Nature*, 1994, **369**, 382.

2 Z. Hiroi, N. Kobayashi and M. Takano, *Nature*, 1994, **371**, 139.

3 C. Q. Jin, X. J. Wu, P. Laffez, T. Tatsuki, T. Tamura, S. Adachi, H. Yamauchi, N. Koshizuka and S. Tanaka, *Nature*, 1995, **375**, 301.

4 P. R. Slater, P. P. Edwards, C. Greaves, I. Gameson, M. E. Francesconi, J. P. Hodges, M. Al-Mamouri and M. Slaski, *Physica C*, 1995, **241**, 151.

5 M. S. Islam and L. J. Winch, *Phys. Rev. B*, 1995, **52**, 10510; L. J. Winch and M. S. Islam, *J. Chem. Soc., Chem. Commun.*, 1995, 1595; M. S. Islam and R. C. Baetzold, *J. Mater. Chem.*, 1994, **4**, 299; *Phys. Rev. B*, 1989, **40**, 10926.

6 N. L. Allan and W. C. Mackrodt, *Adv. Solid State Chem.*, 1993, **3**, 219; X. Zhang, C. R. A. Catlow and W. Zhou, *Physica C*, 1991, **168**, 417.

7 M. S. Islam, D. J. Ilett and S. C. Parker, *J. Phys. Chem.*, 1994, **98**, 9637; M. S. Islam, M. Cherry and L. J. Winch, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 479.

8 M. Leslie, CASCADE code, Daresbury Laboratory, Warrington, 1982.

9 C. R. A. Catlow, in *Solid State Chemistry: Techniques*, ed A. K. Cheetham and P. Day, Clarendon Press, Oxford, 1987.

10 B. G. Dick and A. W. Overhauser, *Phys. Rev.*, 1958, **112**, 90.

11 D. L. Novikov, A. J. Freeman and J. D. Jorgensen, *Phys. Rev. B*, 1995, **51**, 6675.

12 S. D'Arco and M. S. Islam, *Phys. Rev. B*, in the press.

13 J. D. Jorgensen, B. Dabrowski, S. Pei, D. R. Richards and D. E. Hinks, *Phys. Rev. B*, 1989, **40**, 2187.

14 C. Chaillout, S. W. Cheong, Z. Fisk, M. S. Lehmann, M. Marezio, B. Morosin and J. E. Schirber, *Physica C*, 1989, **158**, 183.

15 M. Al-Mamouri, P. P. Edwards, C. Greaves, P. R. Slater and M. Slaski, *J. Mater. Chem.*, 1995, **5**, 913.

Received, 26th July 1996; Com. 6/05248G