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From oxides to oxyhalides: modelling the properties of high T_C superconductors

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Atomistic computer simulation techniques are used to investigate the defect properties of high temperature superconductors, in an attempt to illustrate the type of information that can be obtained from the modelling of these complex materials. Attention is focused on two systems: the mercury cuprate $HgBa_2CuO_{4+\delta}$, which is the first member of the homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$, and the copper oxychloride $Ca_2CuO_2Cl_2$, which is part of a new family of oxyhalide superconductors. Effective interatomic potentials are used to reproduce accurately their observed crystal structures. A range of redox and dopant substitution reactions relevant to high T_C behaviour have been examined. The results are consistent with the experimental observation that $HgBa_2CuO_{4+\delta}$ becomes superconducting by oxygen incorporation at interstitial sites, while $Ca_2CuO_2Cl_2$ shows superconductivity only on doping with alkali metal ions at the calcium site. We also consider the energetics of dopant substitution on the copper sublattice of the oxychloride. Our study indicates the value of computer simulation methods in examining the nature of defect reactions at the atomic level.

The historic discovery of high temperature superconductivity in copper-based oxides has generated considerable interest from both the fundamental and applied perspective because of their potential use in a number of technologies. Since the earliest La_2CuO_4 material,[1] many new families of compounds exhibiting this exotic behaviour have been synthesised with ever-increasing chemical and structural complexity.[2,3] The current record transition temperature (T_C) of 133 K (or 164 K under pressure) is held by $HgBa_2Ca_2Cu_3O_{8+\delta}$, a material whose processing requires the stoichiometric control of five elements.[4,5] It is now well established that the solid state chemistry and defect-related processes play a vital role in determining the properties of superconducting compounds. For example, La_2CuO_4 shows superconducting behaviour when doped with Sr or Ba, whereas the T_C of $YBa_2Cu_3O_{7-\delta}$ is strongly influenced by the degree of oxygen non-stoichiometry.[1–3]

Over the last decade, we and other researchers (notably Allan and Mackrodt) have demonstrated that atomistic simulation techniques, based on effective potentials and Mott–Littleton methodology, can be used to probe the solid-state properties of superconducting oxides that are relevant to their high T_C behaviour.[6–11] These properties include the behaviour of localised species (defects or impurities), and the nature of redox processes responsible for the creation of the itinerant charge-carriers. It is recognised that simulation methods by their nature cannot yield details of the band structures of solids, where electronic structure methodology is the more appropriate technique. They are, however, well suited to probing the defect properties of ceramic oxides on the atomic scale, many of which are difficult to examine by purely experimental techniques.

In an attempt to illustrate the range and type of information that can be obtained by atomistic simulations of increasingly complex materials, we present current modelling work on two systems. The first relates to the mercury cuprate $HgBa_2CuO_{4+\delta}$ which is the first member of the homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ and exhibits the highest T_C (94 K) of any single copper–oxygen layer superconductor.[12,13] Secondly, calculations are reported on $Ca_2CuO_2Cl_2$ which is part of a new family of oxyhalide superconductors[14,15] with the halide ions replacing the apical oxygens in the crystal structures. This compound is of interest because it exhibits p-type superconductivity in an environment where the copper atom is not coordinated entirely by oxygen atoms. One of the significant outcomes of the present study is that it offers an explanation based on calculated energetics as to why particular 'hole doping' mechanisms are found in these two systems. Before discussing the results of our studies we describe briefly the simulation approach employed.

Methodology

The atomistic simulations presented here use the same methodology for the treatment of perfect and defective lattices as employed in previous studies of high-T_C oxides.[6–11] The methods are based upon the specification of an interatomic potential model which expresses the total energy of the system as a function of the atomic coordinates. For ceramic oxides, the calculations are commonly formulated within a Born model representation, with the total energy partitioned into long range Coulomb interactions and analytical pair-potentials to model overlap repulsions and van der Waals forces. Because charge defects will polarise other ions in the lattice, ionic polarisability must be incorporated into the potential model. The shell model[16] provides a simple description of such effects and has proved to be effective in simulating the dielectric and lattice dynamic properties of ceramic oxides.

Static simulations of the perfect lattice evaluate the lattice energy which is then minimised with respect to all relevant structural variables. These determine the low temperature phase, which is particularly relevant in the case of superconducting materials. It should be stressed, as argued previously,[17] that employing such a model does not necessarily mean that the electron distribution corresponds to a fully ionic system, and that the general validity of the potential model is assessed primarily by its ability to reproduce observed crystal properties. In practice, it is found that models based on formal charges work well even for some semi-covalent compounds such as silicates and zeolites.

An important feature of these calculations is the treatment of lattice relaxation about the point defect or dopant ion. The celebrated Mott–Littleton approach[18,19] is to partition the crystal lattice into two regions so that ions in a spherical inner region surrounding the defect are relaxed explicitly. In contrast, the remainder of the crystal, where the defect forces are relatively weak, is treated by more approximate quasicontinuum methods. The explicit simulation of the inner region uses efficient energy minimisation methods which make use of first and second derivatives of the energy function with respect to ion coordinates. We note that these simulation methods are embodied in the CASCADE[20] and GULP[21] programs, and have been applied to a rich variety of polar inorganic solids.[17,19]

There is now ample evidence that given reliable interatomic potentials and a sufficiently large inner region these methods can produce accurate values of the energies of defect formation, migration, and substitution. In the present study, the short-range potential parameters assigned to each ion–ion interaction were derived by empirical fitting to the observed structural properties. All the cuprate superconductors have the same basic crystal structure comprising alternating perovskite blocks of copper–oxygen sheets and rocksalt-like blocks. The mercury cuprate $HgBa_2CuO_{4+\delta}$ adopts a tetragonal unit cell[12] (shown in Plate 1) in which the Cu is six-coordinate to oxygen; the Hg atoms are two-coordinated with the two oxygen atoms arranged in a 'dumb-bell' configuration. For the first three members of the homologous series, namely $HgBa_2CuO_{4+\delta}$,

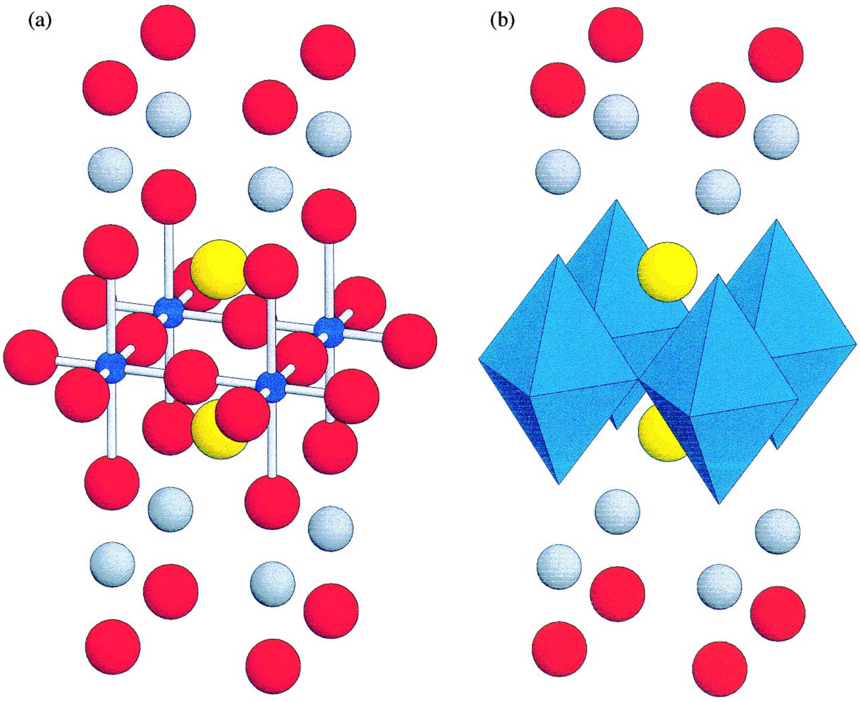

Plate 1 Crystal structure of $HgBa_2CuO_4$ showing (a) atom positions (b) copper–oxygen octahedra (grey = Hg, yellow = Ba, blue = Cu, red = O)

$HgBa_2CaCu_2O_{6+\delta}$ and $HgBa_2Ca_2Cu_3O_{8+\delta}$, the parameters were fitted simultaneously, resulting in a common set of interatomic potentials. This approach enables some information concerning the curvature of the energy surface to be included and has the added advantage of improved transferability. The copper oxyhalide $Ca_2CuO_2Cl_2$ crystallises with the La_2CuO_4-type structure shown in Plate 2; this also has Cu in octahedral coordination but with Cl residing on the apical position.[14,15] Details of the interatomic potentials and shell model parameters are available elsewhere.[7,8] An important test of any theoretical approach to these materials is the accurate simulation of the crystal structures. The calculated and experimental lattice parameters for both $HgBa_2CuO_4$ and $Ca_2CuO_2Cl_2$ are listed in Table 1 which reveal good agreement between simulated and observed structures. In addition, the lattice energy and relative permittivities for the

Table 1 Calculated crystal properties of $HgBa_2CuO_4$ and $Ca_2CuO_2Cl_2$

property	$HgBa_2CuO_4$	$Ca_2CuO_2Cl_2$
lattice parameters/Å[a]		
a	3.936 (3.875)	3.870 (3.869)
c	9.413 (9.513)	15.088 (15.050)
lattice energy/eV	−148.46	−101.65
relative permittivity		
$\langle \varepsilon_0 \rangle$	30.43	18.81
$\langle \varepsilon_\infty \rangle$	6.24	8.13

[a] Observed values in parentheses.

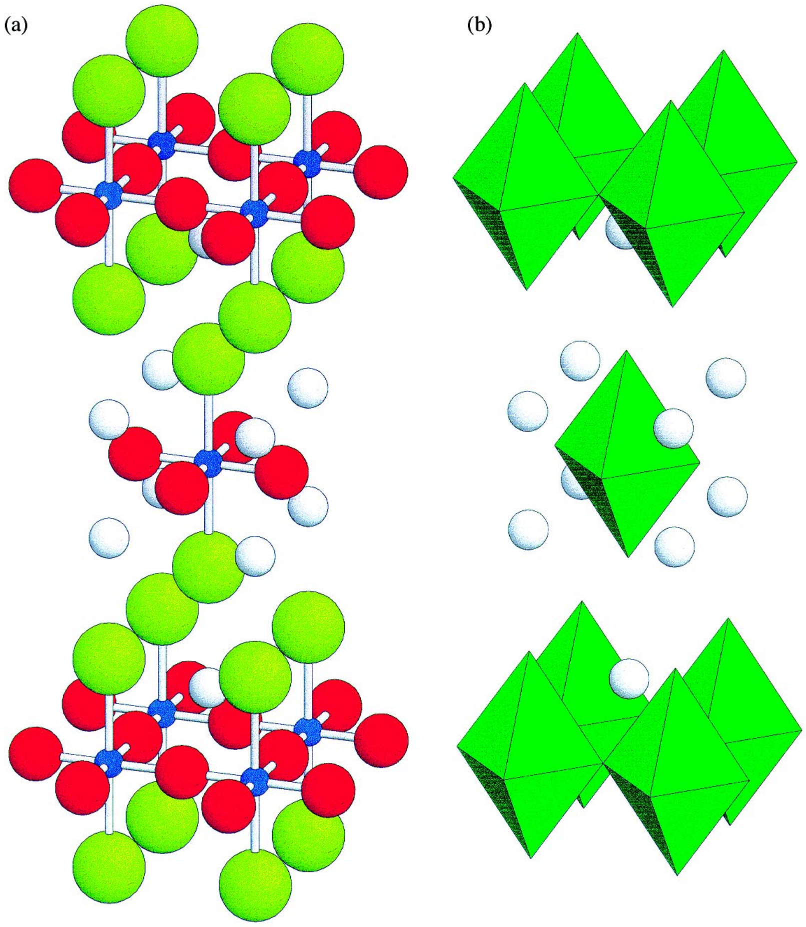

Plate 2 Crystal structure of $Ca_2CuO_2Cl_2$ showing (a) atom positions (b) corner-sharing octahedra (white = Ca, blue = Cu, red = O, green = Cl)

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.

Results and Discussion

Oxidation reactions in $HgBa_2CuO_{4+\delta}$

The Hg-based superconductors have attracted considerable attention owing to their record critical temperatures (T_C). The $HgBa_2CuO_{4+\delta}$ compound[12,13] which has a T_C of 94 K is of particular interest because of its unusually high T_C for a superconductor with a single copper–oxygen layer per unit cell (shown in Fig. 1). In a similar process to $YBa_2Cu_3O_{6+\delta}$, it is generally believed that for $HgBa_2CuO_{4+\delta}$ excess oxygen accommodated at interstitial sites in the HgO_δ layer is the primary hole-doping mechanism for p-type superconductivity.[22] Calculations in this area are amenable by our simulation methods and are particularly suited to evaluating the energetics of defect formation. We therefore address a key issue related to the superconductivity of the $HgBa_2CuO_{4+\delta}$

system, namely the nature of the redox reaction responsible for generating charge carriers.

In terms of defect chemistry, the oxygen excess is incorporated at interstitial sites with charge compensation by hole formation. This important oxidation reaction may be formulated as (1)

$$\tfrac{1}{2}O_{2(g)} \leftrightarrow O_i'' + 2h^{\cdot} \tag{1}$$

where, in Kroger–Vink notation, O_i'' is a doubly charged oxygen interstitial and $h^{\cdot}$ is a hole species. The lowest energy oxygen interstitial site is calculated to be that at ($\tfrac{1}{2}$, $\tfrac{1}{2}$, 0) in the centre of the HgO_δ layer, in agreement with diffraction studies.[12,13] All other interstitial positions in the lattice are found to be greater in energy. Our approach to the investigation of electronic defects follows that first used for transition-metal oxides and subsequently the oxide superconductors.[6–9]. The positive holes are treated in localised terms as Cu^{3+} and O^{-} small polaron species (Table 2). 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. Ultimately, it will be necessary to employ first-principles methods to examine the stability of electronic states in these materials. The merit of our simulation approach is that it includes detailed estimates of lattice polarisation and Coulomb energies which are difficult to make from other sources. The energy of the oxidation reaction (1) was calculated and is reported in Table 2.

The negative value, indicating a highly favourable reaction, clearly accords with observation as it is known that this material readily oxidises with the uptake of oxygen. The calculated oxidation energy is slightly more exothermic than that determined for $YBa_2Cu_3O_{6+\delta}$. Moreover, we find good quantitative agreement with a measured oxidation enthalpy of -110 to -136 kJ mol^{-1} (-1.14 to -1.41 eV) for $HgBa_2CuO_{4+\delta}$ derived from oxygen annealing experiments;[23] this provides encouraging support for the reliability of the potentials and the general validity of our modelling approach. Our results therefore confirm that this reaction is responsible for the generation of charge carriers (holes) necessary for superconductivity in this oxide.

Ionic diffusion (particularly of oxygen) is known to be of considerable importance in influencing the properties of the cuprate superconductors. Although there have been numerous reports on oxygen diffusion in $YBa_2Cu_3O_{6+\delta}$ materials,[24] there are currently

Table 2 Calculated defect energies in $HgBa_2CuO_4$

(a) isolated defect species

defect	energy/eV
oxygen interstitial (O_i'')[a]	−18.20
Cu hole ($h^{\cdot}$)	3.44
O hole ($h^{\cdot}$)	5.32

(b) oxidation process

reaction	energy/eV
$\tfrac{1}{2}O_{2(g)} \leftrightarrow O_i'' + 2h^{\cdot}$	−1.47

[a] Interstitial position at centre of Hg plane ($\tfrac{1}{2}$ $\tfrac{1}{2}$ 0).

no results on oxygen diffusion in the Hg based oxides. We have already obtained *via* simulation methods valuable energetic and mechanistic information on oxygen migration in other high T_C oxides.[6] We have therefore examined possible interstitial migration in $HgBa_2CuO_{4+\delta}$ mediated by conventional hopping between neighbouring sites. This mechanism relates to the direct pathway between interstitial sites in the Hg plane.

The migration energy is evaluated by calculating the defect energy of the mobile oxygen ion along the diffusion path with full lattice relaxation. The resulting activation energy is found to be *ca.* 0.3 eV which suggests facile oxygen diffusion in this material. As remarked earlier, there are at present limited oxygen transport data on Hg-based compounds with which direct comparisons may be made, although our calculated energy is lower than typical values for other superconducting oxides.[24] In view of the favourable interstitial motion in the Hg layer, anisotropic ion transport is anticipated for single crystal $HgBa_2CuO_{4+\delta}$ with high diffusion coefficients (D_{ab}) in the *ab* plane. Indeed such anisotropic transport behaviour is a common feature in other cuprate superconductors.[24]

Defects and dopants in $Ca_2CuO_2Cl_2$

The oxyhalides $Sr_2CuO_2F_{2+\delta}$[25] and $Ca_2CuO_2Cl_2$[14,15] have opened up a new class of cuprate superconductors in which the apical position, above and below the CuO_2 plane, is occupied by a halide ion rather than oxygen. In the case of the $Ca_2CuO_2Cl_2$ compound, which has an La_2CuO_4-type structure and a T_C of 26 K, it is believed that p-type superconductivity is induced by partial substitution of Na^+ for Ca^{2+}. In contrast, high T_C behaviour in $Sr_2CuO_2F_{2+\delta}$ ($T_C = 46$ K) is associated with excess fluorine at interstitial sites. However, some ambiguity still remains concerning the hole-doping reaction in $Ca_2CuO_2Cl_2$ with speculation centred around alternative mechanisms involving either the incorporation of interstitial anions or the partial substitution of oxygen for chlorine.[14] The purpose of this study is to use simulation techniques to investigate further the defect chemistry and mode of hole formation in $Ca_2CuO_2Cl_2$ which extends our previous work on the $Sr_2CuO_2F_{2+\delta}$ system.[8]

The presence of interstitial anions in the $A_2CuO_{4+\delta}$ family of superconductors can be an important contribution to the doping of these materials. For example, interstitial anion defects have been reported for $La_2CuO_{4+\delta}$,[26] $La_2NiO_{4+\delta}$,[27] and more recently, $Sr_2CuO_2F_{2+\delta}$.[25] From structural studies of these materials the interstitial position is found to be $(0, \frac{1}{2}, \approx\frac{1}{4})$ of the tetragonal cell in which the interstitial ion is eight-coordinate. However, neutron powder diffraction studies[15] find no evidence of interstitial anions in $Ca_2CuO_2Cl_2$. To investigate this problem, calculations were performed on isolated chlorine and oxygen interstitials at the ideal position in the $Ca_2CuO_2Cl_2$ 'parent' compound, in which the lattice ions surrounding the defect were allowed to relax in the energy minimisation procedure. The individual point defect energies (interstitial and vacancy) are first combined to give formation energies for Frenkel and Schottky disorder (reported in Table 3). The results show that whilst the chlorine Frenkel energy is lower than the value for the Schottky defect, the magnitude suggests that intrinsic disorder of this type is not significant in the oxychloride.

In relation to superconducting behaviour, we then examined the nature of the oxidation–reduction reaction that may be responsible for the formation of charge carriers. The following redox reactions for $Ca_2CuO_2Cl_2$ were considered: (i) oxidation to form holes from oxygen incorporation as interstitial defects as in $HgBa_2CuO_{4+\delta}$ [eqn. (1)]; (ii) oxidation to form holes from chlorine incorporation as interstitial defects:

$$\tfrac{1}{2}Cl_{2(g)} \leftrightarrow Cl_i' + h^{\bullet} \qquad (2)$$

Table 3 Calculated defect energies in $Ca_2CuO_2Cl_2$

(a) isolated defect species

defect	Energy/eV
O^{2-} interstitial (O_i'')	-13.85
Cl^- interstitial (Cl_i')	0.88
O^{2-} vacancy ($V_O^{\bullet\bullet}$)	24.19
Cl^- vacancy ($V_{Cl}^{\bullet}$)	4.26
Cu^{2+} vacancy (V_{Cu}'')	27.36
Ca^{2+} vacancy (V_{Ca}'')	18.85

(b) intrinsic atomic disorder

defect type	energy/eV per defect
oxygen Frenkel	5.17
chlorine Frenkel	2.57
Schottky	2.90

(iii) oxidation to form holes from partial oxygen substitution of apical chlorine

$$\tfrac{1}{2}O_{2(g)} + Cl_{Cl}^{\times} \leftrightarrow O_{Cl}' + \tfrac{1}{2}Cl_{2(g)} + h^{\bullet} \qquad (3)$$

which is similar to the 'anion doping' mechanism found in the oxychloride (Sr, Ca)$_3$Cu$_2$O$_{4+\delta}$Cl$_{2-y}$ ($T_C = 80$ K); and [28] (iv) reduction to form electrons from partial chlorine substitution of oxygen

$$\tfrac{1}{2}Cl_{2(g)} + O_O^{\times} \leftrightarrow Cl_O^{\bullet} + \tfrac{1}{2}O_{2(g)} + e' \qquad (4)$$

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 Nd_2CuO_4-type compounds that do not possess apical oxygens,[3,32] it should be investigated.

The energies of these four redox reactions in the low temperature limit are collected in Table 4 and were derived using relevant defect and intra-atomic energy terms. Owing to the uncertainties of the free-ion terms, we must be cautious in giving detailed interpretations. Nevertheless, three main points emerge from these results. First, the high positive values for reactions (1) and (2) confirm that these reactions, involving interstitial chlorine or oxygen, are not responsible for the introduction of the holes necessary for superconductivity. This is in accord with neutron powder diffraction studies[15] which find little evidence to support the presence of interstitial anions in $Ca_2CuO_2Cl_2$; their refinements are consistent with the absence of any static displacements that would

Table 4 Calculated energies for redox reactions in $Ca_2CuO_2Cl_2$

process	defects	energy/eV per hole
oxidation:		
reaction (1)	O_i'', $h^{\bullet}$	3.51
reaction (2)	Cl_i', $h^{\bullet}$	4.03
reaction (3)	O_{Cl}', $h^{\bullet}$	2.55
reduction:		
reaction (4)	$Cl_O^{\bullet}$, e'	14.23

suggest additional defects. Further, the Goldsmidt tolerance factor for this material is $t = 1.05$ which would indicate that the Ca_2O_2 layer is under compression and has no capacity to accommodate interstitial atoms, as argued by Argyriou *et al.*[15] By comparison La_2CuO_4 has a tolerance factor of 0.88 which indicates that the La_2O_2 layer is under tension and can readily form interstitial defects within this layer. Second, the high positive value for the reduction reaction (4) involving electron formation suggests that the oxychloride is resistant to n-type behaviour as expected. Finally, it is evident that the oxidation reaction (3) with replacement of apical Cl^- ions by O^{2-} is energetically unfavourable, suggesting that this process is unlikely to be of any significance in this material. The results are therefore fully compatible with the experimental observation that $Ca_2CuO_2Cl_2$, unlike $Sr_2CuO_2F_{2+\delta}$ (or $HgBa_2CuO_{4+\delta}$), does not become superconducting by the incorporation of interstitial anions.

In addition to the redox reactions discussed above, charge carriers may be extrinsically produced by doping with aliovalent cations. Although direct sensitivity to sodium substitution on the calcium site in $(Ca,Na)_2CuO_2Cl_2$ is limited from diffraction studies, it has been concluded that such a substitution is the dominant hole-doping mechanism for high T_C behaviour.[14,15] Our modelling approach is based upon assessing the relative energetics of reaction (or solution) for dopant substitution. Here we have considered the incorporation of a range of alkali-metal ions at both calcium and copper sites in the parent compound $Ca_2CuO_2Cl_2$. The relevant processes can be represented by the following two equations:

$$\tfrac{1}{2}M_2O + Ca_{Ca}^{\times} + \tfrac{1}{4}O_{2(g)} \leftrightarrow M'_{Ca} + h^{\bullet} + CaO \tag{5}$$

$$\tfrac{1}{2}M_2O + Cu_{Cu}^{\times} + \tfrac{1}{4}O_{2(g)} \leftrightarrow M'_{Cu} + h^{\bullet} + CuO \tag{6}$$

where M_2O signifies the dopant oxide and M'_{Ca} (or M'_{Cu}) the dopant substitutional; these reactions indicate that the substitution of either sublattice leads to the creation of holes. The interatomic potentials for the dopant species (given in Table 5) are exactly those of previous studies of corresponding oxides[29] and chlorides.[30] The resulting energies of solution are presented in Table 6 and in Fig. 1 as a plot *vs.* ion size.

The simulations reveal that the alkali dopant ions (except lithium) substitute preferentially for the calcium site. The solution energy for sodium on the calcium site is calculated to be −0.70 eV which is consistent with the observed solubility of Na_2O in $Ca_2CuO_2Cl_2$. Moreover, this result is fully compatible with the proposed hole-doping mechanism in the oxychloride and contrasts with the unfavourable positive energies for the reactions involving anion interstitials (Table 4). We also calculate low solution energies for K^+ and Rb^+ substitution which predict that these doped materials might exhibit high T_C behaviour. Indeed, recent high pressure studies of Tatsuki *et al.*[31] have found p-type superconductivity in the $(Ca,K)_2CuO_2Cl_2$ system. Examination of Fig. 1 reveals that the small lithium ion is calculated to substitute for copper. Although doping with lithium would be predicted to generate holes, cation substitution on the copper

Table 5 Interatomic potentials for dopant species in $Ca_2CuO_2Cl_2$

interaction	A/eV	ρ/Å	C/eV Å^6	Y^+/e	k^+/eV Å^{-2}
$Na^+\cdots O^{2-}$	611.1	0.3535	0.0	2.218	96.41
$Li^+\cdots O^{2-}$	292.3	0.3472	0.0	0.705	7.989
$K^+\cdots O^{2-}$	902.8	0.3698	0.0	−83.55	86032.0
$Rb^+\cdots O^{2-}$	1010.8	0.3793	0.0	−125.3	121460.0
$Na^+\cdots Cl^-$	2314.7	0.2903	29.6	2.218	96.41
$Li^+\cdots Cl^-$	1380.6	0.2786	0.34	0.705	7.989
$K^+\cdots Cl^-$	4117.9	0.3048	124.9	−83.55	86032.0
$Rb^+\cdots Cl^-$	3559.9	0.3233	201.2	−125.3	121460.0

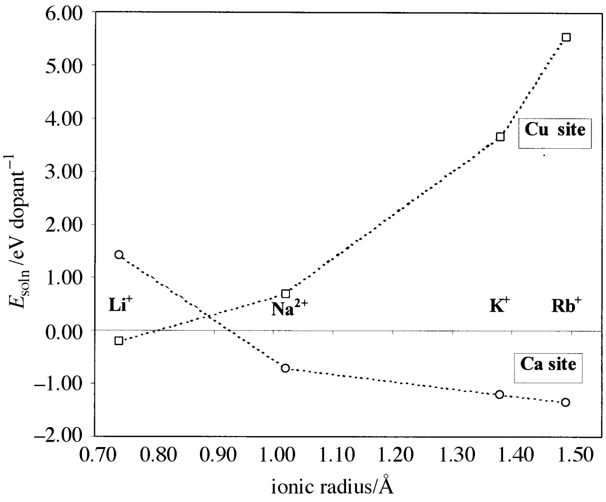

Fig. 1 Calculated solution energies as a function of ion radius for alkali metal dopants at both Ca and Cu sites in $Ca_2CuO_2Cl_2$

sublattice generally does not lead to a high T_C compound since the superconducting copper-oxygen planes are disrupted; this type of deleterious effect on T_C has been observed for dopant substitutions for copper in $YBa_2Cu_3O_7$ and other cuprates.[32]

Conclusion

Atomistic computer simulations have yielded valuable information on fundamental defect properties of oxide and oxyhalide superconductors that are relevant to their high T_C behaviour. The calculated energies are fully compatible with the observation that $HgBa_2CuO_{4+\delta}$ is rendered superconducting by oxygen incorporation at interstitial sites, while $Ca_2CuO_2Cl_2$ exhibits superconductivity only on doping with alkali metal ions (*e.g.* Na^+, K^+). These results are in accord with powder diffraction studies which find no evidence of interstitial anions in $Ca_2CuO_2Cl_2$. We also find good agreement with the measured oxidation energy for $HgBa_2CuO_{4+\delta}$. The simulations therefore allow us to rationalise, based on quantitative calculations as opposed to qualitative arguments, why particular reactions are responsible for the creation of charge carriers. It is recognised that there are limitations to such an approach to certain problems where the use of explicit electronic structure techniques may be more appropriate. Current studies,

Table 6 Calculated solution energies of dopants at both Ca and Cu sites in $Ca_2CuO_2Cl_2$

	solution energy/eV per dopant	
dopant ion	E_{Ca}	E_{Cu}
Li^+	1.43	−0.20
Na^+	−0.70	0.69
K^+	−1.20	3.67
Rb^+	−1.35	5.55

however, demonstrate the value (and versatility) of simulation methods in probing the nature of defect-related processes in complex solids.

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References

1 J. G. Bednorz and K. A. Muller, *Z. Phys. B: Condens. Matter*, 1986, **64**, 189.
2 M. A. E. Aranda, *Adv. Mater.*, 1994, **6**, 905.
3 R. J. Cava, *Science*, 1990, **247**, 656.
4 A. Schilling, M. Cantoni, J. D. Gao and H. R. Ott, *Nature* (*London*), 1993, **363**, 56.
5 C. W. Chu, L. Gao, F. Chen, Z. J. Huang, R. L. Meng and Y. Y. Yue, *Nature* (*London*), 1993, **365**, 323.
6 M. S. Islam, M. Leslie, S. M. Tomlinson and C. R. A. Catlow, *J. Phys. C.*, 1988, **21**, L1085; M. S. Islam and R. C. Baetzold, *Phys. Rev. B.*, 1989, **40**, 10926; *J. Mater. Chem.*, 1994, **4**, 299.
7 M. S. Islam and L. J. Winch, *Phys. Rev. B.*, 1995, **52**, 10510; *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1595.
8 M. S. Islam and S. D'Arco, *Chem. Commun.*, 1996, 2291; *Phys. Rev. B.*, 1997, **55**, 3141.
9 N. L. Allan and W. C. Mackrodt, *Adv. Solid State Chem.*, 1993, **3**, 219; *J. Am. Ceram. Soc.*, 1990, **73**, 3175.
10 X. Zhang and C. R. A. Catlow, *J. Mater. Chem.*, 1991, **1**, 233; *Physica C.*, 1991, **173**, 25.
11 R. C. Baetzold, *Phys. Rev. B.*, 1988, **38**, 11304; *Mol. Sim.*, 1994, **12**, 77.
12 S. N. Putilin, E. V. Antipov, O. Chmaissem and M. Marezio, *Nature* (*London*), 1993, **362**, 226.
13 J. L. Wagner, P. G. Radaelli, D. G. Hinks, J. D. Jorgensen, J. F. Mitchell, B. Dabrowski, G. S. Knapp and M. A. Beno, *Physica C*, 1993, **210**, 447.
14 Z. Hiroi, N. Kobayashi and M. Takano, *Nature* (*London*), 1994, **371**, 139.
15 D. N. Argyriou, J. D. Jorgensen, R. L. Hitterman, Z. Hiroi, N. Kobayashi and M. Takano, *Phys. Rev. B*, 1995, **51**, 8434.
16 B. G. Dick and A. W. Overhauser, *Phys. Rev.*, 1958, **112**, 90.
17 C. R. A. Catlow in *Solid State Chemistry: Techniques*, ed. A. K. Cheetham and P. Day, Clarendon Press, Oxford, 1987.
18 N. F. Mott and M. T. Littleton, *Trans. Faraday Soc.*, 1938, **34**, 485.
19 *J.Chem. Soc.*, *Faraday Trans 2.*, 1989, **85**, 335–579.
20 M. Leslie, CASCADE code, Daresbury Laboratory, UK, 1982.
21 J. D. Gale, *J. Chem. Soc.*, *Faraday Trans.*, 1997, **93**, 629.
22 M. A. Subramanian and M. H. Whangbo, *J. Solid State Chem.*, 1994, **109**, 410.
23 Q. Xiong, Y. Y. Xue, F. Chen, Y. Gao, Y. Y. Sun, L. M. Liu, A. J. Jacobson and C. W. Chu, *Physica C*, 1994, **231**, 233.
24 J. L. Routbort and S. J. Rothman, *J. Appl. Phys.*, 1994, **76**, 5615.
25 M. Al-Mamouri, P. P. Edwards, C. Greaves and M. Slaski, *Nature* (*London*), 1994, **369**, 382.
26 C. Chaillout, S. W. Cheong, Z. Fisk, M. S. Lehman, M. Marezio, B. Morosin and J. E. Schirber, *Physica C*, 1989, **158**, 183.
27 J. D. Jorgensen, B. Dabrowski, S. Pei, D. R. Richards and D. E. Hinks, *Phys. Rev. B*, 1989, **40**, 2187.
28 C. Q. Jin, X. J. Wu, P. Laffez, T. Tatsuki, T. Tamura, S. Adachi, H. Yamauchi, N. Koshizuka and S. Tanaka, *Nature* (*London*), 1995, **375**, 301.
29 G. V. Lewis and C. R. A Catlow, *J. Phys. C.*, 1985, **18**, 1149; *J. Phys. Chem. Solids*, 1986, **47**, 89.
30 C. R. A. Catlow, K. M. Diller and M. J. Norgett, *J. Phys. C.*, 1977, **10**, 1395.
31 T. Tatsuki, S. Adachi, M. Itoh, T. Tatura, X. J. Wu, C. Q. Jin, N. Koshizuka and K. Tanabe, *Physica C.*, 1995, **255**, 61.
32 C. N. R. Rao and B. Raveau, *Acc. Chem. Res.*, 1989, **22**, 106.

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