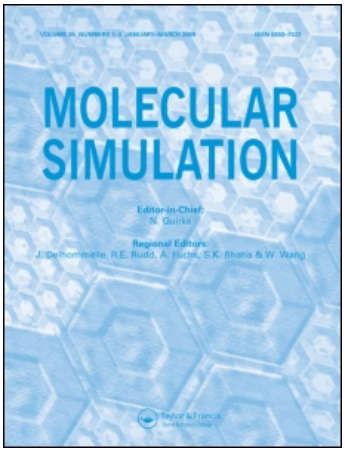

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OXYGEN INTERSTITIAL DEFECTS IN HIGH-T_c OXIDES

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Atomistic lattice calculations are reported of the energetics associated with the formation of oxygen interstitial defects in La_2CuO_4, Nd_2CuO_4, $LaNdCuO_4$, and $YBa_2Cu_3O_6$. The location and charge state of the additional oxygen are considered and hole-interstitial association energies estimated. The last of these varies considerably from system to system. The implications for the high-T_c behaviour of these materials, including the effects of fluorination on La_2CuO_4 and Nd_2CuO_4, are discussed in detail.

KEY WORDS: High-T_c oxides, oxygen interstitial defects

INTRODUCTION

In all the known high temperature superconductors the charge carriers are extrinsically controlled. These can be produced either by doping with aliovalent impurities (as with $La_{1.85}Sr_{0.15}CuO_4$ [1] and $Nd_{1.85}Ce_{0.15}CuO_4$ [2]) or by oxidation (as in $La_2CuO_{4.13}$ [3–5] and $YBa_2Cu_3O_{6+x}$ [6]). In previous work [7] the first of these modes was examined in detail together with the defect chemistry of the ternary cuprates M_2CuO_4 (M = La,Nd) using well-established computational methods. Oxidation and, in particular, the possible role of oxygen interstitial defects in these systems, was not considered.

Subsequent to our initial studies [7] it has been established [3–5] that the *Fmmm* oxygen-rich phase of lanthanum cuprate, La_2CuO_{4+y}, prepared by high pressure/high temperature treatment of La_2CuO_4, has a T_c ($\approx$38 K) comparable to that of $La_{2-x}Sr_xCuO_4$. However, there has been some controversy concerning the nature of the excess oxygen into the lattice. Early reports of bulk superoxide (O_2^-) [8] have been disputed [9] on the grounds that much of the excess oxygen is superficial, for homogeneous samples with high oxygen content appear to be virtually impossible to achieve due to spontaneous phase separation below 320 K [3]. The high temperature electrical conductivity and Seebeck coefficient measurements of Su *et al.* [10] support the presence of doubly charged oxygen interstitials, while Jorgensen *et al.* [11] have reported neutron diffraction data for the isomorphous

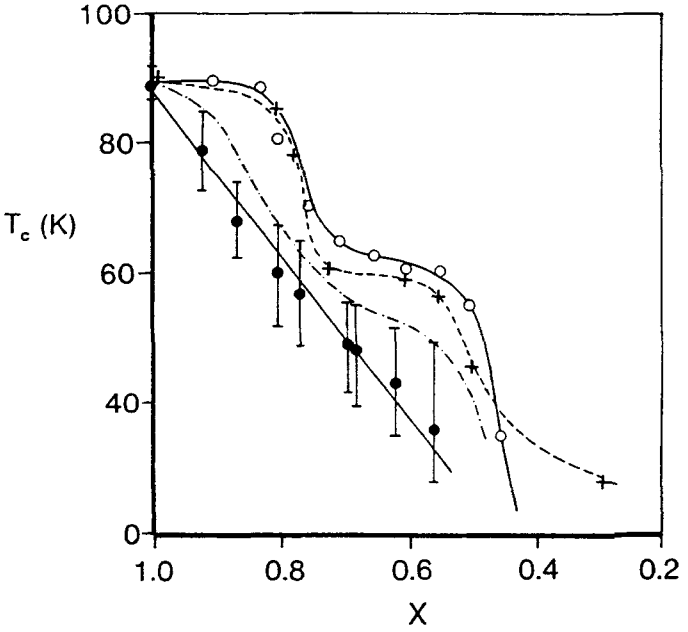

Figure 1 Variation of T_c with oxygen content X for differently prepared samples of $YBa_2Cu_3O_{6+X}$ samples (after reference 12). Closed circles - reference 12; open circles - reference 13; + – – + – reference 14; – · – · – · – reference 15.

compound La_2NiO_{4+X} that, for the *Fmmm* phase at least, are consistent with interstitials of this type but preclude the larger peroxide or superoxide ions.

In view of these diverse interpretations of oxygen excess in La_2CuO_4, a further examination based on atomistic lattice calculations might be of value. Accordingly, in the present paper we report calculated energies of oxygen interstitial defects in La_2CuO_4 and, for completeness, in Nd_2CuO_4 and $LaNdCuO_4$, which are representative of ternary cuprates with the so-called T' and T^* structures respectively.

In the presence of even a small amount of excess oxygen La_2CuO_{4+X} is superconducting [4]; for example, T_c for $La_2CuO_{4.13}$ is 34 K [4]. In contrast, it is clear from Figure 1, which shows the variation of T_c with oxygen content for $YBa_2Cu_3O_{6+X}$ reported by several groups [12–15], that this system is not superconducting for $X < \approx 0.3$, irrespective of the means of sample preparation. On the other hand, $Y_{1-Z}Ca_ZBa_2Cu_3O_6$ has a reported $T_c \approx 50$ K [16, 17]. In this work, therefore, we also compare oxygen incorporation in La_2CuO_4 and $YBa_2Cu_3O_6$ in an attempt to rationalise this intriguing behaviour.

The crystal structures of all the systems for which calculations are reported here are shown in Figure 2. La_2CuO_4, Nd_2CuO_4 and $LaNdCuO_4$ contain CuO_2 planes in which the Cu is six-, four- and five-fold coordinated to oxygen respectively. $YBa_2Cu_3O_6$ possesses a double layer of CuO_5 pyramids and also two-fold coordinated Cu.

Table 1 Calculated defect and redox energies (eV) involving doubly and singly charged oxygen interstitials in tetragonal La_2CuO_4, orthorhombic La_2CuO_4 and Nd_2CuO_4.

	Tetragonal La_2CuO_4	*Orthorhombic* La_2CuO_4	Nd_2CuO_4
Defect energies:			
O_i''	−13.89	−13.40	−14.66
O_i'	−1.60	−0.89	−3.22
Schottky energy (per defect)	1.5	1.9	2.6
Frenkel energy (per defect)	1.1	1.6	1.5
Redox energies:			
$E_1\ \frac{1}{2}O_2(g) = O_i'' + 2h^{\cdot}$	0.7	1.7	3.1
$E_2\ O_i'' = O_i' + e'$	5.8	5.7	1.4

THEORETICAL METHODS

The atomistic simulations reported here use the same ionic model and the identical methodology for the treatment of perfect and defective lattices as employed previously [6]. Charges are assigned to ions according to usual chemical valence rules, e.g 2+ for copper, calcium and strontium, 2− for lattice oxygen, 3+ for lanthanum and neodymium. Two-body, electron-gas potentials [18] are used to specify non-Coulombic interactions and the Dick-Overhauser shell model [19] included to allow for the effects of electronic polarization.

An advantage of the ionic model is the straightforward identification of valence band holes as Cu^+ or O^- and defect electrons as Cu^+, while the terms which contribute to the formation energies of these species have been discussed previously [6]. In the present context they are required to estimate the energetics of the redox processes involving the gain or loss of $O_2(g)$. One advantage of the use of non-empirical potentials potentials is that it is straightforward to obtain a Hartree-Fock electron density for O^- and hence derive a set of interatomic potentials for this species. Cation potentials are assumed to be independent of charge state.

The treatment of the defective lattice follows the customary two-region approach [20]. The total energy of the defective system is minimised by means of a relaxation of the nuclear positions (and shell displacements) around the defect. The relaxation is assumed to be greatest close to the defect. The crystal is partitioned into an inner region, which immediately surrounds the defect, and an outer region. In the former the elastic equations for the force are solved explicitly in order to determine the relaxations. In the outer region these are estimated using the Mott-Littleton approximation [21]. In the present work it has been possible to consider inner region radii over 50% ($\approx 3a_O$) larger than those used in our previous studies [6] and consequently, some of the values reported here differ slightly from those presented earlier. As before [6], the Kroger-Vink notation is used throughout to describe lattice and electronic defects.

La_2CuO_4, Nd_2CuO_4 and $LaNdCuO_4$

Table 1 lists calculated defect energies for singly charged and doubly charged oxygen interstitials in the tetragonal and orthorhombic phases of La_2CuO_4 and

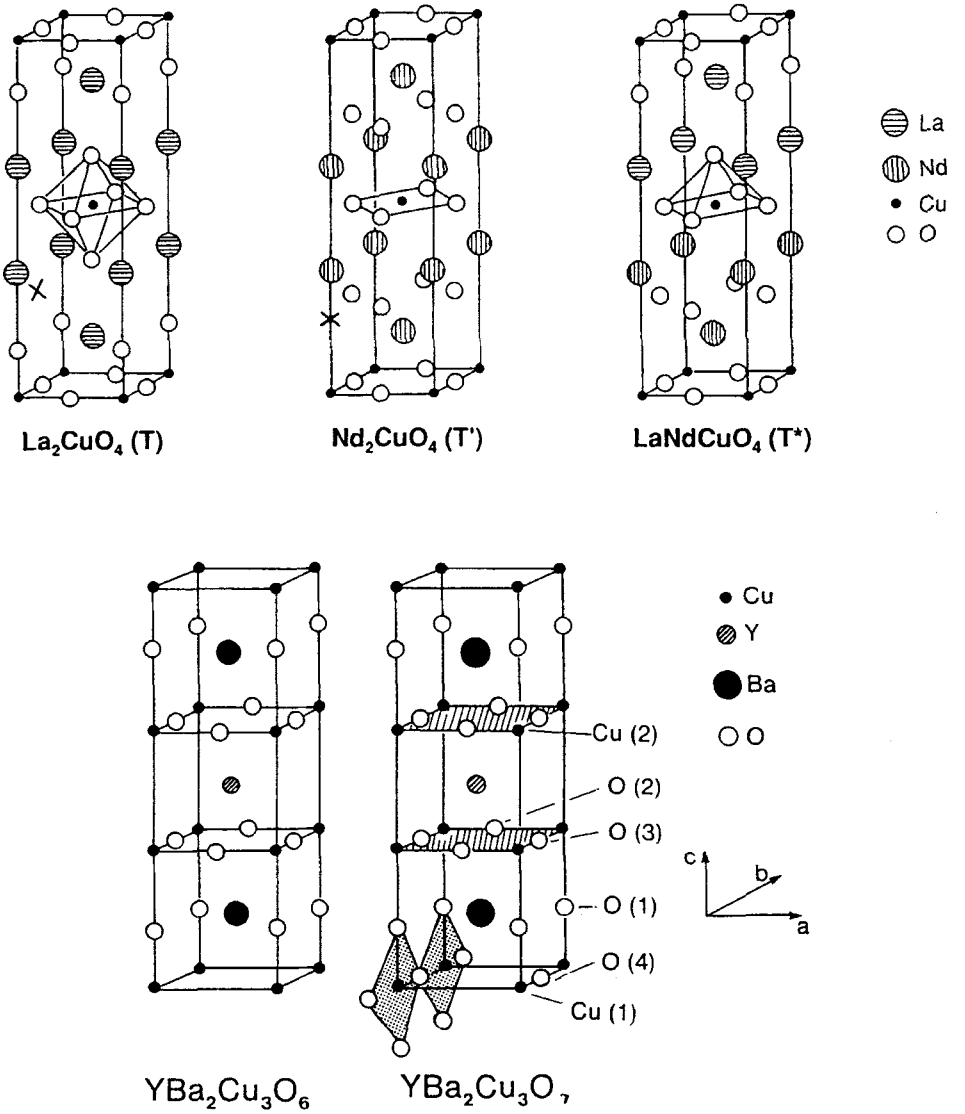

Figure 2 The crystal structures of tetragonal La_2CuO_4, Nd_2CuO_4, $LaNdCuO_4$, $YBa_2Cu_3O_6$, and $YBa_2Cu_3O_7$. In La_2CuO_4 and Nd_2CuO_4 the lowest energy interstitial position is marked with crosses.

also in Nd_2CuO_4. In each case the lowest energy interstitial position is marked with a cross in Figure 2. This position is favoured over all others we have examined by at least 1 eV. In La_2CuO_4, the postulated positions, $((0,1/2,\approx 1/4)$ in the tetragonal phase and $(1/4,1/4,\approx 1/4)$ in the orthorhombic, both with four nearest La neighbours, agree with that suggested by the neutron diffraction studies of Chaillout *et al.* [22], and that occupied by the excess oxygen in La_2NiO_{4+Y} [11].

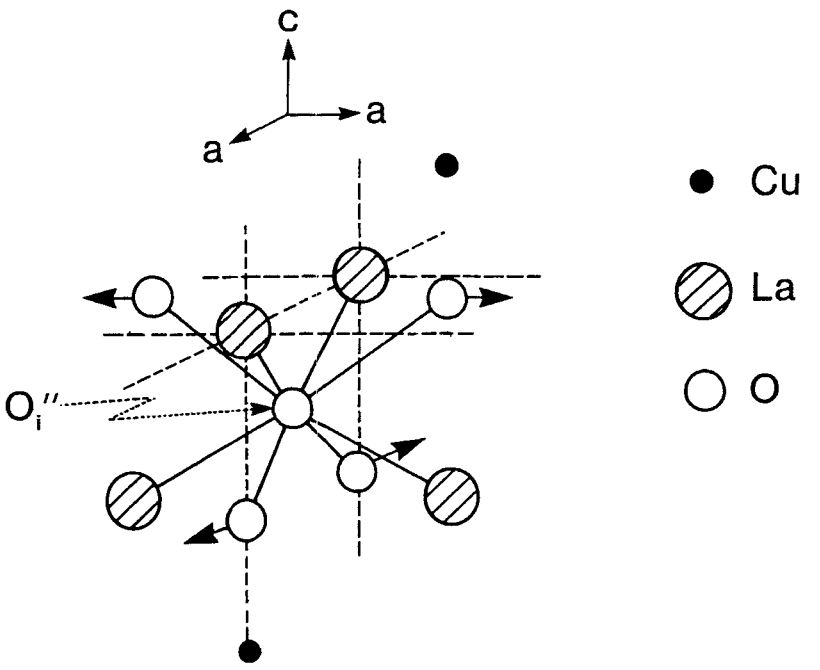

Figure 3 The calculated local environment surrounding a doubly charged oxygen interstitial in La_2CuO_4. The calculated interionic separations are La – O ≈ 2.3 Å, O – O ≈ 2.7 Å.

It is also in agreement with the simulations of Zhang *et al.* [23] who employed three-body empirical potentials rather than the non-empirical two-body potentials used here. In La_2CuO_4 the four nearest oxygens are displaced about 0.5 Å from their normal lattice sites away from the doubly charged interstitial; the calculated distance between these and the interstitial is 2.7 Å (see Figure 3). This local relaxation is close to that reported for $La_2NiO_{4+\gamma}$ [11]. However, the neutron diffraction studies of $La_2CuO_{4+\gamma}$ [22] indicate one short (interstitial O)-(lattice O) distance of < 1.8 Å for which we are unable to account; it could possibly indicate a complex involving an oxygen interstitial and a hole on one of the nearest-neighbour oxygens.

In the case of Nd_2CuO_4 the lowest energy interstitial position is $(0,0,\approx 1/4)$. In the La_2CuO_4 and Nd_2CuO_4 structures the favoured position is a site occupied by an oxide ion in the other.

The calculated Frenkel energies per defect for tetragonal La_2CuO_4, orthorhombic La_2CuO_4 and Nd_2CuO_4 are 1.09 eV, 1.56 eV and 1.46 eV respectively. Whilst these are lower than the corresponding values for Schottky defects (Table 1), the magnitudes suggest only a small degree of intrinsic disorder in the absence of oxygen. This contrasts with results obtained previously for Sr_2CuO_3 and Ca_2CuO_3 [24]. In the latter systems, which contain one-dimensional CuO_2 chains rather than two-dimensional CuO_2 planes, calculated anion Frenkel defects are lower in energy than in La_2CuO_4 and Nd_2CuO_4 with values of −0.1 eV and 0.4 eV per defect for Sr_2CuO_3 and Ca_2CuO_3 respectively.

Also listed in table 1 are the calculated energies, E_1 and E_2 respectively, for the important redox reactions:

$$\frac{1}{2} O_2(g) = O_i'' + 2h^{\cdot} \tag{1}$$

and

$$O_i'' = O_i' + e' \tag{2}$$

We have assumed that the first and second ionisation energies for interstitial oxygen are the same as those for lattice oxygen and have used previously reported values [6]. Likewise, the formation energies of electronic defects were those estimated in earlier work [6, 25–27].

From the values of E_1 and E_2 doubly charged interstitials are predicted in both materials and a $p(O_2)$ dependence of 1/6 for $[h^{\cdot}]$, as suggested by the high-temperature conductivity measurements of Su *et al.* [10]. In addition E_1 for Nd_2CuO_4 is considerably larger than that for La_2CuO_4. This implies that Nd_2CuO_4 will exhibit a substantially smaller range of oxygen excess than La_2CuO_4, which also appears to be the case. An analysis of the component energies shows that even though the calculated oxygen interstitial energy in Nd_2CuO_4 is lower than that in La_2CuO_4, E_1 is larger as a result of a considerably larger hole formation energy, 3.1 eV as against 1.5 eV in La_2CuO_4 [6, 25–27].

The formation of doubly charged oxygen interstitials compensated by holes is consistent with the occurrence of superconductivity in La_2CuO_{4+Y} since holes are thought to be a necessary prerequisite for high temperature superconductivity in the La-Cu-O system. Furthemore, the maximum value of T_c occurs for $X \approx 0.15$–0.2 in $La_{2-X}Sr_XCuO_4$, and for $Y \approx 0.08$–0.1 in La_2CuO_{4+Y}, which is entirely consistent with the proposed mode of oxygen incorporation since oxygen excess leads to twice the hole concentration of an equivalent excess (doping) of Sr.

Nd_2CuO_4 exhibits superconductivity apparently only via defect electrons. Consequently, oxygen-rich material would not be expected to be superconducting, and indeed our results suggest that excess oxygen will inhibit superconductivity. This is consistent with the finding that superconductivity in $Nd_{2-X}Ce_XCuO_4$ appears only after a very small amount of oxygen is lost after heat treatment in a reducing atmosphere (e.g, reference 28) which might reasonably be interpreted as the loss of residual oxygen excess.

In the course of this work we also investigated the possible incorporation of peroxide (O_2^{2-}) and superoxide (O_2^-) into La_2CuO_4, but were unable to find any minima in the relevant potential-energy surfaces consistent with the formation of these species. Zhang *et al.* [23] have also estimated formation energies of O_2^{2-} and O_2^- in La_2CuO_4 and found them to be considerably greater than that for the incorporation of oxygen as $O_i^{\cdot}$. The present and previous [23] studies, therefore, concur with the conductivity measurements of Su *et al.* [10] which preclude the formation of superoxide and peroxide at elevated temperatures. However, we note that confirmation of one mode of incorporation at high temperature does not rule out an alternative or competing mechanism at low temperatures.

In the case of hole superconductors such as La_2CuO_4, it is important to consider the possibility of hole trapping by the negatively charged oxygen interstitials. We have evaluated the association energies for a number of defect complexes in

tetragonal La_2CuO_4 consisting of a single oxygen interstitial and one or two copper and oxygen holes in a variety of configurations. These association energies, which are relative to the energy of an "isolated" oxygen interstitial and that of the corresponding free carriers, are all small (typically a few tenths of an eV) and *positive* for holes in the CuO_2-planes, indicating a net repulsion between the holes and the interstitials (due to relaxation effects). The association energy between the interstitial and two nearest neighbour oxygen holes is calculated to be negative (≈ -0.35 eV per hole). However, this value is much less than the energy difference between such oxygen holes and copper holes in the superconducting planes. It is suggested, therefore, that holes will not be trapped by interstitials in La_2CuO_4. These results are similar to those found in previous work [6] where it was established that holes are not trapped by divalent or monovalent impurities.

Several groups (e.g., references 29, 30) have reported the preparation of a superconducting compound ($T_c \approx 40$ K) by the direct fluorination of La_2CuO_4. Superconductivity has also been observed in $Nd_2CuO_{4-x}F_x$ (e.g., references 31, 32), prepared by the action of heat on a mixture of Nd_2O_3, NdF_3 and CuO. Two important reactions involving fluorine are:

$$\frac{1}{2}F_2(g) = F_i' + h^{\cdot} \tag{3}$$

and

$$\frac{1}{2}F_2(g) + O_0^x = F_0^{\cdot} + \frac{1}{2}O_2(g) + e' \tag{4}$$

The first would lead to *p*-type (super)conductivity, the latter to *n*-type behaviour.

First estimates of the energies of these two reactions can be obtained by equating the lattice energy contributions to the formation of interstitial and lattice fluoride are those for O^-, i. e. $E(F_i') \approx E(O_i')$ and $E(F_0^{\cdot}) \approx E(O_0^{\cdot})$. With these and the further assumption that the ionization potential of lattice F^- is that of the free gaseous ion, energies, E_3 and E_4, for reactions 3 and 4 can be estimated. At 1000 K, which is roughly the synthesis temperature of these systems, there is also a significant contribution to the total free energy from the entropy of gaseous fluorine. Assuming the defect energies are essentially independent of temperature, we estimate E_3 and E_4 to be -1.5 eV and 1.4 eV respectively for tetragonal La_2CuO_4 at 1000 K. The corresponding values for Nd_2CuO_4 are -1.5 eV and -2.0 eV respectively.

Despite the numerous assumptions made in arriving at estimates of E_3 and E_4, the implications of these values are clear. Fluorination of La_2CuO_4 is expected to lead to the incorporation of interstitial fluoride ions and holes leading to *p*-type (super)conductivity. In this context it is also worth noting that superconductivity has been observed in chlorine-treated La_2CuO_4 [33], presumably due to a similar mechanism. In contrast, the fluoridation of Nd_2CuO_4 is expected to lead to fluoride ion substitution and the formation of defect electrons, leading to *n*-type conductivity (cf., the Ce^{4+} doping of Nd_2CuO_4 to give $Nd_{2-x}Ce_xCuO_4$). Previous calculations on Nd_2CuO_4 [7] have found the energy of $E(O_0^{\cdot})$ defects to be only 0.1 eV lower in the Nd-O planes than in the CuO_2 planes, so that it is tentatively suggested that substitution by F^- will take place at both sites. The location of the fluoride ions has, of course, important implications for any theory of

high-temperature superconductivity. The experimental evidence is ambiguous (see the discussion in reference 34). As emphasised elsewhere [26, 27], the differing behaviour of La_2CuO_4 and Nd_2CuO_4 is due largely to the difference in the relative formation energies of defect electrons and holes, which in turn have been linked to the different copper coordinations in the two systems.

Finally in this section we consider briefly the location of oxygen interstitials in the T^* structure, as illustrated by $LaNdCuO_4$. Figure 2 shows that the T^* structure is a hybrid of the La_2CuO_4 (T) and Nd_2CuO_4 (T') structures in that the unit cell is half T-type and half T'-type. Cu is solely fivefold coordinate while there are two *inequivalent* lanthanide sites - 9-coordinate (RE) in the T-like half of the unit cell and 8-coordinate (RE′) sites in the T' half. Calculations reported elsewhere [27], on $LaNdCuO_4$ indicate a preferential occupation of the RE and RE′ sites by La^{3+} and Nd^{3+} respectively. With reference to Figure 2, the calculated defect energies of double charged oxygen interstitials in this structure at $(0, 0, \approx 0.25)$ and $(0, 0.5, \approx 0.75)$ are -13.6 and -14.6 eV respectively. This suggests, somewhat surprisingly in view of the relative interstitial energies in La_2CuO_4 and Nd_2CuO_4 themselves, that the energy of the interstitial in the T half of the structure is lower in energy than that in the T' section. This is in agreement with the neutron diffraction experiments of Lightfoot *et al.* [35] which indicated that interstitial oxygen in the T^* structure adopted by $La_{1.25}Dy_{0.75}CuO_{3.75}F_{0.5}$ was located in the T unit.

INCORPORATION OF OXYGEN IN $YBa_2Cu_3O_6$

We now turn to the incorporation of oxygen in $YBa_2Cu_3O_6$, the "parent" oxide of $YBa_2Cu_3O_{7-X}$ which was the first system found to possess a T_c (≈ 90 K) at liquid nitrogen temperatures [36]. With reference to Figure 2, $YBa_2Cu_3O_7$ can be considered formally as derived from semiconducting $YBa_2Cu_3O_6$ by the introduction of oxygen into the vacant O(4) site. $YBa_2Cu_3O_6$ possesses Cu atoms in two different environments - 5-coordinate Cu in the CuO_2 planes and 2-coordinate Cu. Electronic structure [37] and previous atomistic simulation studies [27, 38] indicate that these are in different oxidation states - the former Cu(II), the latter Cu(I).

As is the case with La_2CuO_{4+X}, the charge carriers in $YBa_2Cu_3O_{6+X}$ are formed not by aliovalent substitution of the trivalent cation but by oxygen incorporation. We have already alluded to the fact that the variation of T_c with oxygen content X in $YBa_2Cu_3O_{6+X}$ [12–15], shown in Figure 1, is of particular theoretical interest. There appear to be considerable differences between samples prepared by different techniques, and, in particular, between those prepared by quenching from high temperature and those formed by the low temperature reduction of $YBa_2Cu_3O_7$. Nevertheless it is generally accepted that high T_c behaviour does not occur for $X < \approx 0.3$. In contrast, superconductivity has been observed at ≈ 50 K in $Y_{1-Z}Ca_ZBa_2Cu_3O_6$ [16, 17], in which the charge carriers are introduced by the substitution of Y^{3+} by Ca^{2+}, as in $La_{2-X}Ca_XCuO_4$. Furthermore, the superconducting properties of $Yb_{1-Z}Ca_Z(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+X}$, reported recently by Wada *et al.* [39], are very similar to those of $Y_{1-Z}Ca_ZBa_2Cu_3O_{6+X}$, in that these systems are superconducting even for very small values of X.

Calculated hole formation energies in $YBa_2Cu_3O_6$ [27, 38] suggest the lowest energy *free carrier* to be a Cu hole in the (super)conducting CuO_2 planes (Cu(2)), with a formation energy of ≈ 2.6 eV. Oxygen holes in the CuO_2 planes are pre-

dicted to be broadly similar in energy (≈3.3 eV) as are holes at the O(1) apical position (≈2.8 eV), allowing for the uncertainties associated with the terms contributing to the total formation energy. Holes at the Cu(1) position, on the other hand, are calculated to have considerably higher energies.

The lowest energy oxygen interstitial site is found to be that at O(4) in the basal plane, in agreement with experiment. In this position the interstitial is *strongly* bound to two neighbouring Cu(1) holes (i.e two Cu^{2+} ions). All other configurations of the oxygen interstitial and the two holes are found to be *much* greater in energy.

The calculated energy, E_1 of ≈ -0.5 eV, for the incorporation of oxygen at the O(4) site,

$$\frac{1}{2}O_2(g) = O_i'' + 2h^{\cdot} \qquad O_i'' \equiv O_{O(4)}^{\cdot}$$

is lower than that in La_2CuO_4 and compares with the experimental value of ≈ -1.0 eV [40, 41]. The strong interstitial-hole association in $YBa_2Cu_3O_6$ contrasts with that in La_2CuO_4, in which interstitial oxygen is stabilised by four nearest-neighbour La^{3+} ions, and, as a result, appears to show no tendency to bind to holes in the CuO_2 plane.

Our calculations suggest that the absence of superconductivity in $YBa_2Cu_3O_{6+X}$ for $X < \approx 0.3$ can be accounted for by the prediction that holes resulting from the excess oxygen, O_X, are trapped in the basal plane adjacent to the O(4) position, as opposed to being free carriers in the CuO_2 planes, in broad agreement with Goodenough's view [42]. In $Y_{1-Z}Ca_ZBa_2Cu_3O_6$, on the other hand, the basal plane contains neither lattice nor interstitial oxygen, so that holes introduced by Ca^{2+} will be located, at least partially, in the CuO_2 planes leading to superconductivity. This would appear to be a plausible explanation for high T_c behaviour in Ca-doped materials with oxygen content less than ≈6.3 [16, 17]. As in La_2CuO_4, the calculated association energy between Ca_Y and holes in the CuO_2 planes is very small, which contrasts markedly with the strong association predicted for basal plane holes and O(4).

In summary, then, the different locations of interstitial oxygen in La_2CuO_4 and $YBa_2Cu_3O_6$ have been shown to have important implications for the superconducting behaviour of these two systems. Calculations on oxygen incorporation in $YBa_2Cu_3O_{6+X}$ for $X > 0.3$ will be reported elsewhere.

CONCLUSIONS

This paper has concentrated on the incorporation of oxygen in high temperature superconducting oxides. The location of the excess oxygen, the energetics of the process and the hole-interstitial association energies appear to have important consequences for the high-T_c properties. All of these differ significantly from one crystal structure to another.

It is suggested that excess oxygen can be incorporated in both La_2CuO_4 and Nd_2CuO_4 as doubly charged oxygen interstitials. The favoured position in each of these structures is close to a site occupied by an oxide ion in the other. Compensation of the negatively charged oxygen interstitials by holes provides an explanation

of the high temperature superconducting properties of oxygen-rich La_2CuO_{4+Y}. The results can also be used to rationalise why the fluorination of La_2CuO_4 leads to *p*-type superconductivity, whilst $Nd_2CuO_{4-X}F_X$ is an *n*-type material.

In $YBa_2Cu_3O_6$, excess oxygen enters the basal plane and is strongly bound to holes located in this plane. This suggests an explanation for the lack of superconductivity in $YBa_2Cu_3O_{6+X}$ for $X < \approx 0.3$ and the high-T_c properties of $Y_{1-Z}Ca_Z Ba_2Cu_3O_6$.

$La_2CaCu_2O_6$ has the same double layer of CuO_5 bipyramids as $YBa_2Cu_3O_{6+X}$ and all the superconducting oxides with the highest T_c's. T_c's of $\approx$60 K and $\approx$45 K have now been reported for $La_{1.6}Sr_{0.4}CaCu_2O_6$ [43] and $La_{1.85}Ca_{1.15}Cu_2O_6$ [44] respectively. Preliminary results for this system [45] indicate that oxygen interstitials will be located between the CuO_5 pyramids which provide the CuO_2 (super)conducting planes, unlike $YBa_2Cu_3O_6$.

In conclusion, atomistic lattice simulations have been used to highlight the importance of the defect chemistry associated with oxygen interstitial defects in high-T_c oxides. The calculations are relatively simple, but provide an specific approach to this problem that is highly versatile.

Acknowledgements

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References

[1] For example, T. Fujita and Y. Maeno, "Preparation and property of $La_{1.85}Sr_{0.15}CuO_4$ single crystal," *Japan J. Appl. Phys.*, **26**, L386 (1987).

[2] Y. Tokura, H. Takagi and S. Uchida, "A superconducting copper oxide compound with electrons as the charge carriers," *Nature*, **337**, 345 (1989).

[3] J.D. Jorgensen, B. Dabrowski, Shiyou Pei, D.G. Hinks, L. Soderholm, B. Morosin, J.E. Schirber, E.L. Venturini, and D.S. Ginley, "Superconducting phase of $La_2CuO_{4+\delta}$," *Phys. Rev.*, **B38**, 11337 (1988).

[4] J.E. Schriber, B. Morosin, R.M. Merrill, P.F. Hlava, E.L. Venturini, J.F. Kwak, P.J. Nigrey, R.J. Baughman, and D.S. Ginley, "Stoichiometry of bulk superconducting $La_2CuO_{4+\delta}$: a superconducting superoxide?" *Physica*, **C152**, 121 (1988).

[5] G. Demazeau, F. Tresse, Th. Plante, J. Chevalier, J. Etourneau, C. Michel, M. Hervieu, B. Raveau, P. Lejay, A. Sulpice, and T. Tournier, "Evolution of the superconducting properties in the La_2CuO_4 lattice versus oxygen pressure," *Physica*, **C153-155**, 824 (1988).

[6] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Q. Wang, and C.W. Chu, "Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure," *Phys. Rev. Lett.*, **58**, 908 (1987).

[7] For example, N.L. Allan and W.C. Mackrodt, "The calculated defect properties of La_2CuO_4 related to high-T_c superconductivity," *Phil. Mag.*, **A58**, 555 (1988); N.L. Allan. J.M. Lawton and W.C. Mackrodt, "A comparison of the calculated lattice and defect structures of La_2CuO_4, La_2NiO_4, Nd_2CuO_4, Pr_2CuO_4, Y_2CuO_4, Al_2CuO_4," *Phil. Mag.*, **B59**, 191 (1989).

[8] J.W. Rogers Jr., N.D. Shinn, J.E. Schirber, E.L. Venturini, D.S. Ginley, and B. Morosin, "Identification of a superoxide in superconducting $La_2CuO_{4+\delta}$ by X-ray photoelectron spectroscopy," *Phys. Rev.*, **B38**, 5021 (1988).

[9] J. Zhou, S. Sinha, J.B. Goodenough, "Comment on 'Identification of a superoxide in superconducting $La_2CuO_{4+\delta}$ by X-ray photoelectron spectroscopy' ", *Phys. Rev.*, **B39**, 12331 (1989).

[10] M.-Y. Su, E.A. Cooper, C.E. Elsbernd, and T.O. Mason, "High-temperature defect structure of lanthanum cuprates." *J. Am. Ceram. Soc.*, **73**, 453 (1990).

[11] J.D. Jorgensen, B. Dabrowski, S. Pei, D.R. Richards, and D.G. Hinks, "Structure of the

interstitial oxygen defect in $La_2NiO_{4+\delta}$," *Phys. Rev. B*, **40**, 2187 (1989).
[12] C. Namgung, J.T.S. Irvine and A.R. West, "Absence of critical temperature plateau in quenched samples of $YBa_2Cu_3O_X$," *Physica*, **C168**, 346 (1990).
[13] R. Beyers, B.T. Ahn, G. Gorman, V.Y. Lee, S.S.P. Parkin, M.L. Ramirez, K.P. Roche, J.E. Vazquez, T.M. Gur and R.A. Huggins, "Oxygen ordering, phase separation and the 60 K and 90 K plateaus in $YBa_2Cu_3O_X$," *Nature*, **340**, 619 (1989).
[14] R.J. Cava, A.W. Hewat, B. Batlogg, M. Marezio, K.M. Rabe, J.J. Krajewski, W.F. Peck Jr. and L.W. Rupp Jr., "Structural anomalies, oxygen ordering and superconductivity in oxygen deficient $Ba_2YCu_3O_X$," *Physica*, **C165**, 419 (1990).
[15] W.E. Farneth, R.K. Bordia, E.M. McCarron III, M.K. Crawford and R.B. Flippen, "Influence of oxygen stoichiometry on the structure and superconducting transition temperature of $YBa_2Cu_3O_X$," *Solid State Commun.*, **66**, 953 (1988).
[16] E.M. McCarron III, M.K. Crawford and J.B. Parise, "Observation of superconductivity in $(Y_{1-X}Ca_X)Ba_2Cu_3O_6$," *J. Solid State Chem.*, **78**, 192 (1989).
[17] C. Legros Glédel, J.F. Marucco, E. Vincent, D. Favrot, B. Poumellec, B. Touzelin, M. Gupta and H. Alloul, "Influence of the oxygen content on the critical temperature T_c and the thermopower of $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_Z$," *Physica*, **C175**, 279 (1991).
[18] N.L. Allan, D.L. Cooper and W.C. Mackrodt, "The practical calculation of interionic potentials in solids using electron gas theory," *Mol. Sim.*, **4**, 269 (1990). The details of the potentials used in the present paper are available from the authors on request.
[19] B.G. Dick and A.W. Overhauser, "Theory of dielectric constants of alkali halide crystals," *Phys. Rev.*, **112**, 90 (1958).
[20] C.R.A. Catlow and W.C. Mackrodt, "Theory of simulation methods for lattice and defect energy calculations in crystals," in "Computer Simulation of solids" edited by C.R.A. Catlow and W.C. Mackrodt, pp 3–20, Springer-Verlag, Berlin (1982).
[21] N.F. Mott and M.T. Littleton, "Conduction in polar crystals. I. Electrolytic conduction in solid salts," *Trans. Faraday Soc.*, **34**, 485 (1938).
[22] C. Chaillout, S.W. Cheong, Z. Fisk, M.S. Lehmann, M., Marezio, B. Morosin, and J.E. Schirber, "The crystal structure of superconducting $La_2CuO_{4.032}$ by neutron diffraction," *Physica*, **C158**, 183, (1989); erratum, ibid., **C159**, 892 (1989).
[23] X. Zhang, C.R.A. Catlow and W. Zhou, "The determination of the defect states in undoped superconducting La_2CuO_4 by computer simulation techniques," *Physica*, **C168**, 417 (1990).
[24] N.L. Allan, J.M. Lawton, and W.C. Mackrodt, "Calculated crystal and defect properties of ternary cuprates M_2CuO_3 (M = Ca,Sr): Relationship to La_2CuO_4 and high-T_c superconductivity," *J. Phys. Condensed Matter*, **1**, 2657 (1989).
[25] N.L. Allan and W.C. Mackrodt, "Atomistic simulation of high-T_c oxides," *J. Amer. Ceram. Soc.*, **73**, 3175 (1990).
[26] N.L. Allan and W.C. Mackrodt, "Simulation studies of structural and defect properties of high temperature superconducting materials," *Adv. Solid St. Chem.*, **3**, 219 (1993).
[27] N.L. Allan, P.S. Baram, W.C. Mackrodt and M.J. Turner, "Differences between high-T_c oxides containing six-, five-, four- and two-fold coordinated copper," *Mol. Sim.*, **9**, 115 (1992).
[28] N.A. Fortune, K. Murata, M. Ishibashi, Y. Yokoyama and Y. Nishihara, "Systematic variation of transport and thermodynamic properties with degree of reduction in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$," *Phys. Rev.*, **B43**, 12930 (1991).
[29] B.M. Tissue, K.M. Cirillo, J.C. Wright, M. Daeumlling and D.C. Larbalestier, "Conversion of $La_2CuO_{4-\delta}$ to a superconductor by treatment in fluorine gas," *Solid State Commun.*, **65**, 51 (1988).
[30] B. Chevalier, A. Tressaud, B. Lepine, K. Amine, J.M. Dance, L. Lozano, E. Hickey and J. Etourneau, "Stabilization of a new superconducting phase by low temperature fluorination of La_2CuO_4," *Physica*, **C167**, 97 (1990).
[31] A.C.W.P. James, S.M. Zahurak and D.W. Murphy, "Superconductivity at 27 K in fluorine-doped Nd_2CuO_4," *Nature*, **338**, 240 (1989).
[32] J. Sugiyama, M. Kosuge, Y. Ojima, H. Yamauchi and S. Tanaka, "TEM observation and Hall measurement on superconductive $Nd_2CuO_{4-X}F_X$," *Physica*, **C179**, 131 (1991).
[33] A. Tressaud, C. Robin, B. Chevalier, L. Lozano and J. Etourneau, "Superconductivity in chlorine-treated La_2CuO_4," *Physica*, **C177**, 330 (1991).
[34] J. Sugiyama, R. Itti, H. Yamauchi, N. Koshizuka and S. Tanaka, "Photoelectron spectroscopy study of $Nd_2CuO_{4-X}F_X$," *Phys. Rev.*, **B45**, 4952 (1992).
[35] P. Lightfoot, S. Pei, J.D. Jorgensen, X.-X. Tang, A. Manthiram and J.B. Goodenough, "Interstitial anions in the T* structure," *Physica*, **C169**, 15 (1990).

[36] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Q. Wang, and C.W. Chu, "Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure," *Phys. Rev. Lett.*, **58**, 908 (1987).

[37] W.M. Temmerman, Z. Szotek, P.J. Durham, G.M. Stocks and P.A. Sterne, "Electronic structure of Y-Ba-Cu oxides and fluorides," *J. Phys.*, **C17**, L319 (1987).

[38] N.L. Allan, M.J. Turner, A.L. McLean and W.C. Mackrodt, "The calculated crystal and defect chemistry of $YBa_2Cu_3O_6$," *Ceram. Trans.*, **24**, 277 (1991).

[39] T. Wada, Y. Yaegashi, A. Ichinose, H. Yamauchi, and S. Tanaka, "Control of the hole concentration in the $YBa_2Cu_3O_{6+Z}$-type superconductors (Yb, Ca) $(Ba, Sr)_2Cu_3O_{6+Z}$ with low and high Ca contents," *Phys. Rev.*, **B44**, 2341 (1991).

[40] M.E. Parks, A. Navrotsky, K. Mocala, E. Takayama-Muromachi, A. Jacobson and P.K. Davies, "Direct calorimetric determination of energetics of oxygen in $YBa_2Cu_3O_X$," *J. Solid State Chem.*, **79**, 53 (1989).

[41] H. Verweij, W.H.M. Bruggink, R.A. Steeman, E. Frikkee and R.B. Helmholdt, "Oxidation enthalpy of $YBa_2Cu_3O_{6+Y}$ in relation with phase behaviour and stoichiometry," *Physica*, **C166**, 372 (1990).

[42] J.B. Goodenough, "Chemical and structural relationships in high-T_c materials," *Supercond. Sci. Technol.*, **3**, 26 (1990).

[43] R.J. Cava, A. Santoro, J.J. Krajewski, R.M. Fleming, J.V. Waszczak, W.F. Peck Jr. and P. Marsh, "The crystal structure of the $La_{1.6}Sr_{0.4}CaCu_2O_{6+\delta}$ superconductor," *Physica*, **C172**, 138 (1990).

[44] For example, K. Kinoshita, H. Shibata and T. Yamada, "Crystal structure and superconducting properties of $La_{1.85}Ca_{1.15}Cu_2O_{6+\delta}$," *Physica*, **C176**, 433 (1991).

[45] N.L. Allan, P.S. Baram and W.C. Mackrodt, "The calculated crystal and defect chemistry of $RE_2MCu_2O_6$ (RE = La, Nd; M = Ca, Sr)", in preparation.