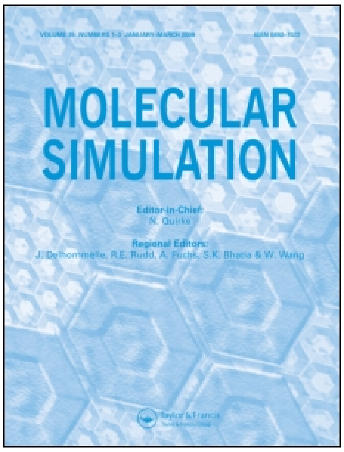

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# Differences Between High-*T<sub>c</sub>* Oxides Containing Six-, Five-, Four- And Two-Fold Coordinated Copper

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# DIFFERENCES BETWEEN HIGH-$T_C$ OXIDES CONTAINING SIX-, FIVE-, FOUR- AND TWO-FOLD COORDINATED COPPER

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Atomistic simulation techniques are used to investigate the defect properties and redox energies of a series of ternary cuprates with different copper coordinations to oxygen. In particular, results are reported for $La_2CuO_4$, $LaNdCuO_4$, $Nd_2CuO_4$, $Y_2CuO_4$ and $YBa_2Cu_3O_6$, amongst others. The implications for the high-temperature superconducting behaviour of these oxides when made non-stoichiometric are discussed in detail. We compare "hole" and "electron" superconductors. In addition we suggest that the variation of $T_C$ with oxygen content, $X$, for $YBa_2Cu_3O_{6+X}$ and $Y_{1-Z}Ca_ZBa_2Cu_3O_{6+X}$ is linked to the two very different environments of Cu in this system.

KEY WORDS: Superconducting oxides, defects, lattice simulation

## 1 INTRODUCTION

Since the historic discovery of high temperature superconductivity in $La_2CuO_4$ ($T_C \approx 30\,K$) [1], and subsequently in other oxides, most attention has been focussed on the details of possible coupling mechanisms. The ceramic properties of these systems have attracted considerably less discussion. It has been shown in earlier work [2–5] by ourselves and others that atomistic lattice simulations of the type used to examine conventional ceramics can be used to calculate important normal-state properties of high-$T_C$ oxides which are clearly relevant to superconducting behaviour. Recent studies of $La_2CuO_4$ and $Nd_2CuO_4$ [2–4], for example, have highlighted differences between the calculated defect chemistry of these two materials which can be used to rationalise why the former cuprate exhibits superconductivity apparently only via holes and the latter only via electrons.

In the present paper we consider a wide range of cuprates with different copper coordinations and relate their defect properties to their superconducting behaviour. Particular attention is paid to the "parent" oxides $La_2CuO_4$ (6-coordinate Cu), $LaNdCuO_4$ (5-coordinate Cu), $Nd_2CuO_4$ (4-coordinate Cu) and $YBa_2Cu_3O_6$ (both 2- and 5-coordinate Cu). All of these systems are made superconducting by aliovalent substitution of $La^{3+}/Nd^{3+}/Y^{3+}$. Of these four cuprates $Nd_2CuO_4$ is the only electron superconductor (when doped with $Ce^{4+}$ or $Th^{4+}$) whilst the remainder are hole superconductors (when oxidised or doped with $Ca^{2+}$ and other divalent cations). We also present results for $Y_2CuO_4$ which has been synthesised recently at high pressure [6] and possesses the same crystal structure as $Nd_2CuO_4$. Finally, the different variations of $T_C$ with oxygen content, $X$, for $YBa_2Cu_3O_{6+X}$ and $Y_{1-Z}Ca_ZBa_2Cu_3O_{6+X}$

are discussed and linked tentatively to the two very different environments of Cu in this system.

## 2 THEORETICAL METHODS

Static simulations of perfect and defective lattices reported here are based on methods similar to those used in recent studies of high-$T_C$ oxides [2–5] and also, somewhat earlier, for a wide range of ceramic oxides [7]. The calculations are formulated within the ionic model, in which ions are assigned charges in accord with the accepted rules of chemical valence, e.g., 2+ for Cu, 2− for O, 3+ for La, Nd or Y. One of the advantages of the ionic model is that it enables a simple definition of valence band holes in terms of $Cu^{3+}$ or $O^-$ and defect electrons as $Cu^+$. Two-body, electron-gas potentials [8] are used consistently [4] to specify the non-Coulombic interactions between the ions and the Dick-Overhauser shell model [9] incorporated to allow for the treatment of the electronic polarisation of the lattice.

The static simulations of perfect lattices give the crystal structure and lattice energy of the low-temperature phase. At 0 K, the lattice structure is determined by the condition that it is in mechanical equilibrium, i.e.,

$$\partial E/\partial X_i = 0$$

in which $E$ is the internal energy, and the $\{X_i\}$ are the variables that define the structure – the lattice vectors, the atomic positions in the unit cell, and, in the case of the shell model, the shell displacements. The last of these represent the electronic polarization of those ions which are not at a centre of inversion symmetry in the lattice and, for polarizable ions such as $O^{2-}$ or $Ba^{2+}$, can make an appreciable contribution to the internal energy.

The treatment of the defective lattice follows the usual two-region approach [10]. The essential idea is the minimisation of the total energy of the defective system by a relaxation of the nuclear positions (and shell displacements) around the defect. The relaxation is assumed to be largest close to the defect and to fall off fairly quickly with distance. The crystal is divided into an inner region, immediately surrounding the defect, and an outer region. In the former the elastic equations for the force are solved explicitly to obtain the relaxations. In the outer region these are estimated using an approximation originally due to Mott and Littleton [11].

## 3 CRYSTAL STRUCTURES

Elements of the perovskite structure, which provide the putative superconducting 2-dimensional $CuO_2$ planes, appear to be essential for high-temperature superconductivity in cuprate systems. Copper ions in these planes can be 6-coordinate ($La_2CuO_4$, $Bi_2Sr_2CuO_6$), 5-coordinate ($LaNdCuO_4$, $YBa_2Cu_3O_6$) or 4-coordinate ($Nd_2CuO_4$): the corresponding crystal structures are shown in Figure 1. The highest $T_C$'s appear to be associated with a double layer of $CuO_5$ pyramids in which the Cu is 5-coordinate. This unit is found in $YBa_2Cu_3O_{6+X}$ and also, for example, in $Bi_2Sr_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$, but not in $La_2CuO_4$ nor $Nd_2CuO_4$.

As shown in Figure 1 $YBa_2Cu_3O_7$ also possesses 1-dimensional $CuO_2$ chains in which the Cu is 4-coordinate. Accordingly we have also studied $Sr_2CuO_3$ [12], in

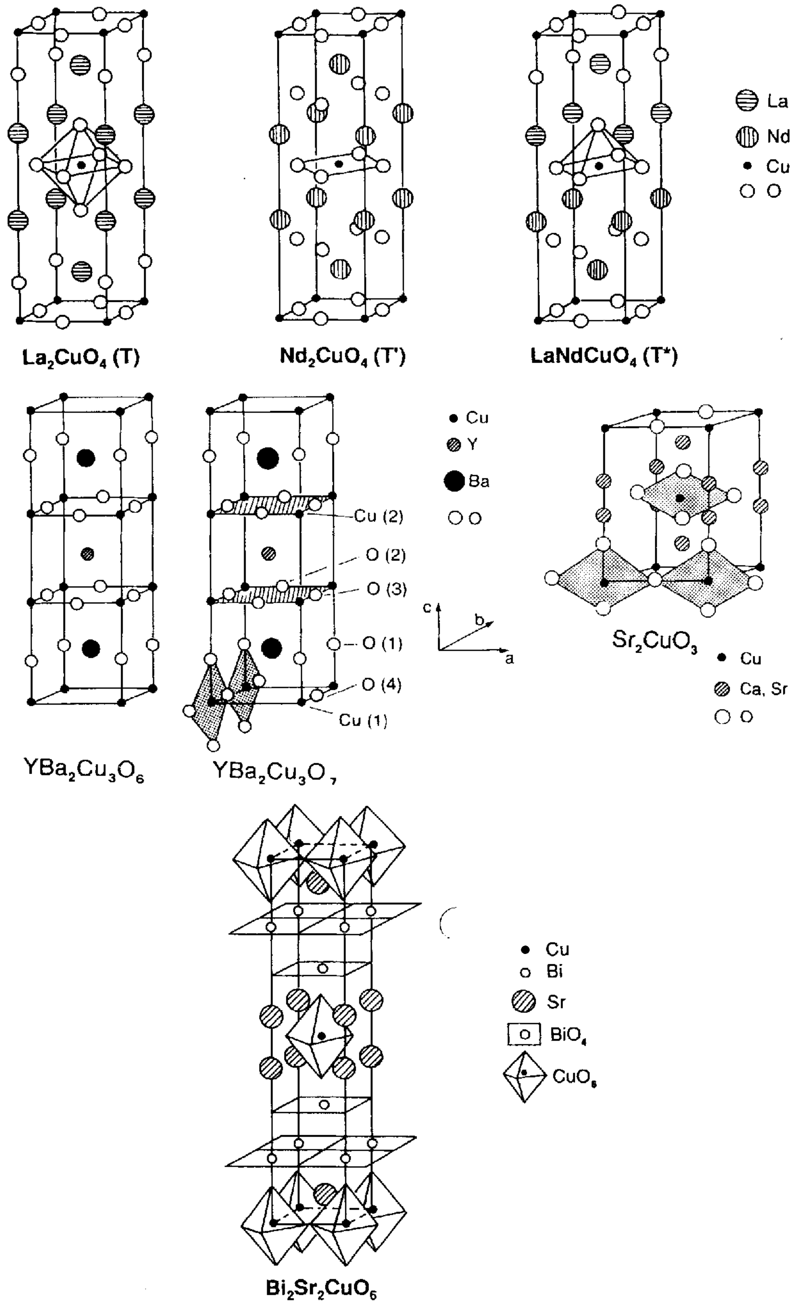

**Figure 1** The crystal structures of tetragonal $La_2CuO_4$ ($T$), $LaNdCuO_4$ ($T^*$), $Nd_2CuO_4$ ($T'$), $Sr_2CuO_3$, $Bi_2Sr_2CuO_6$, $YBa_2Cu_3O_6$, and $YBa_2Cu_3O_7$. In $YBa_2Cu_3O_7$ the 2-dimensional $CuO_2$ planes are shown hatched and the 1-dimensional $CuO_2$ chains shaded; the Cu and O atom labelling used is also shown.

**Table 1** Calculated and experimental lattice constants of tetragonal $La_2CuO_4$, orthorhombic $La_2CuO_4$, $LaNdCuO_4$, $Nd_2CuO_4$, $Sr_2CuO_3$, $Y_2CuO_4$, and $YBa_2Cu_3O_6$. Experimental values are in parentheses.

| *Oxide* | *Structural type* | | *Lattice constants (Å)* | | |
|---|---|---|---|---|---|
| | | | $a_0$ | $b_0$ | $c_0$ |
| $La_2CuO_4$ | Orthorhombic | $K_2NiF_4$ | 5.427 | 5.352 | 12.994 |
| | | | (5.406) | (5.370) | (13.150) [40] |
| $La_2CuO_4$ | Tetragonal | $K_2NiF_4$ ($T$) | 3.783 | – | 13.050 |
| | | | (3.778) | | (13.093) [41] |
| ($La_2CuO_4$ | $T^*$ | | 3.880 | | 12.415)# |
| ($La_2CuO_4$ | $Nd_2CuO_4$ | | 3.972 | | 11.999)# |
| $LaNdCuO_4$ | $T^*$ | | 3.880 | | 12.42 |
| | | | (3.891) | | (12.46) [13]* |
| $Nd_2CuO_4$ | $Nd_2CuO_4$ ($T'$) | | 3.898 | – | 11.985 |
| | | | (3.939) | | (12.147) [42] |
| $Y_2CuO_4$ | $Nd_2CuO_4$ | | 3.830 | – | 11.57 |
| | | | (3.864) | – | (11.70) [6] |
| $Sr_2CuO_3$ | $Sr_2CuO_3$ | | 3.892 | 3.474 | 13.07 |
| | | | (3.91) | (3.48) | (12.69) [43] |
| $Bi_2Sr_2CuO_6$ | $Bi_2Sr_2CuO_6$ | | 3.724 | – | 25.00 [44] |
| | | | (3.79) | | (24.62) [45] |
| $YBa_2Cu_3O_6$ | $YBa_2Cu_3O_6$ | | 3.900 | – | 11.82† |
| | | | (3.854) | | (11.82) [18] |

†Calculated using different Cu(1)–O and Cu(2)–O potentials. See the text.

*The reported lattice constants are for $La_{1.2}Nd_{0.8}CuO_4$.

#Phases not observed experimentally.

which 2-dimensional $CuO_2$ planes are absent and the structure consists solely of such $CuO_2$ chains.

An important test of any theoretical approach to these materials is the accurate calculation of the crystal structures. Table 1 lists the computed and experimental lattice constants of tetragonal $La_2CuO_4$, $Nd_2CuO_4$, $Bi_2Sr_2CuO_6$, $Y_2CuO_4$ and $Sr_2CuO_3$ in which it is seen that calculated lattice constants are within 2% of the measured values for all of these compounds.

Bringley *et al.* [13] have determined the structures and lattice constants of the systems $La_{2-X}Nd_XCuO_4$ $(0 \leqslant X \leqslant 2)$. For $X < \approx 0.4$, the $La_2CuO_4$, or so-called $T$, structure is adopted in which the Cu is 6-coordinate and the lanthanide 9-coordinate to oxygen. For $X > \approx 0.5$ the $Nd_2CuO_4$ $T'$ structure dominates, in which the Cu is 4-coordinate and the lanthanide 8-coordinate to O. In the transformation from $T$ to $T'$, $c_0$ decreases while $a_0$ increases, a trend which is also reproduced in the calculated lattice constants. In addition the different $c_0/a_0$ ratios of the $La_2CuO_4$ and $Nd_2CuO_4$ structures are reproduced. For $Nd_2CuO_4$ the experimental and calculated values of $c_0/a_0$ are 3.08 and 3.07 respectively; for $La_2CuO_4$ the corresponding values are 3.47 and 3.45.

In the region $X \approx 1.0$, a third phase is observed together with the $T$ and $T'$ structures, namely the $T^*$ structure. As is clear from Figure 1, this is a hybrid of $T$ and $T'$ in that the unit cell is half $T$-type and half $T'$-type. Cu is fivefold coordinate and there are two inequivalent lanthanide sites – 9-coordinate $M$ sites in the $T$-like half of the unit cell and 8-coordinate $M'$ sites in the $T'$ half. Our calculations on $LaNdCuO_4$ indicate a preferential occupation of the $M$ and $M'$ sites by La and Nd respectively. The difference in lattice energy between this arrangement and that in which Nd occupies $M$, La $M'$ sites is $\approx 0.4$ eV. The calculated lattice constants for the lowest energy structure are listed in Table 1, together with the experimental values for $La_{1.2}Nd_{0.8}CuO_4$ reported by Bringley *et al.* [13]. Lanthanum and rare-earth site ordering has also been observed [14, 15] in the $T^*$ phases adopted by $La_{2-X-Y}R_XSr_YCuO_4$ ($R$ = Sm, Eu, Gd, Tb). However, the difference in the radii of the two lanthanide ions in these systems is larger than in the case of La and Nd ($r(La^{3+}) \approx 1.20$ Å, $r(Nd^{3+}) \approx 1.16$ Å, $r(Sm^{3+}) \approx 1.09$ Å [16]), and this mismatch will favour such an ordering.

To consider the effects of a change in structure without a change in chemical composition, we have also computed lattice constants (Table 1) for $La_2CuO_4$ itself in the $T^*$ and $T'$ structures. These phases have not been observed for this compound. The qualitative variations of $a_0$, $c_0$ and the $c_0/a_0$ ratio from one structure to another are the same as those reported for the different structures in the $La_{2-X}Nd_XCuO_4$ system.

Figure 1 also shows the structures of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$. In these materials Cu is 5-coordinate to O in the $CuO_2$ planes with O(1), the apical oxygen, part of both the $CuO_5$ pyramids and the Cu–O chains. In $YBa_2Cu_3O_6$ the O(4) and O(5) sites in the "basal" plane are unoccupied, whilst the Cu(1) position in this plane is 2-fold linearly coordinated to O. Since Cu(1) and Cu(2) have different environments it is important to establish the charge state of copper at these two sites. In doing this we have assumed identical short range interionic potentials to those used to investigate $La_2CuO_4$, $Y_2CuO_4$, $Y_2Cu_2O_5$, and $Y_2BaCuO_5$ [2–4, 17]. In systems such as these, the presence of a single Cu sublattice in conjunction with charges based on accepted chemical valence leads to the normal assignment of $+2$ for Cu (and $-2$) for O. However, for systems such as $YBa_2Cu_3O_{6+X}$, in which there are inequivalent Cu sublattices, a number of different assignments of charge are possible within an overall charge balance between cations and anions. In this case of $YBa_2Cu_3O_6$, the lattice energy for an assignment of charges of $+1$ and $+2$ to Cu(1) and Cu(2) respectively is over 6 eV lower than that for an equal assignment of $+5/3$ to both sublattices. The calculated value of $a_0$ (3.900 Å) is within 1.2% of experiment (3.854 Å) [18] and that of $c_0$ (11.59 Å) is 2% smaller than that observed (1.182 Å) [18]. These results suggest the presence of both linearly-coordinated Cu(I) and pyramidally-coordinated Cu(II) which is entirely consistent with the band structure calculations of, for example, Temmerman *et al.* [19].

In view of the lower charge and coordination of Cu(1) it is not unreasonable that the Cu(1)–O short-range potential should be somewhat more repulsive than the Cu(2)–O potential. This suggests a small modification of the former, $V_{Cu(1)\text{-}O}(R)$, which we have implemented simply by writing,

$$V_{Cu(1)\text{-}O}(R) \;=\; V_{Cu(2)\text{-}O}(R - R_0)$$

in which $R_0$ is positive and determined empirically by fitting to the experimental value of $c_0$. The calculated value of $a_0$ is essentially unchanged by this procedure. As discussed later, the very different charges on the Cu ions are crucial in determining the defect and consequently the superconducting properties of $YBa_2Cu_3O_{6+X}$.

## 4 ELECTRONIC DEFECTS AND REDOX BEHAVIOUR

The nature and energetics of the electronic defects are major factors which control the properties of high temperature superconductors. $La_2CuO_4$ ($T$ structure and 6-coordinate Cu) leads to "hole" superconductors either by partial substitution of La by Ca, Sr, Ba or Na to give materials of the type $La_{2-X}Sr_XCuO_4$ [20], or by oxidation to form

$La_2CuO_{4+X}$ [21, 22]. Compounds with the $T'$ structure (4-coordinate Cu), on the other hand, lead to "electron" superconductors when doped with either 4+ cations or $F^-$ ions to give materials such as $Nd_{1.85}Ce_{0.15}CuO_4$ [23] and $Nd_2CuO_{3.6}F_{0.4}$ [24]. Like $T$ structures, $T^*$ systems (5-coordinate Cu) only superconduct when doped $p$-type, as in $Nd_{1.32}Sr_{0.41}Ce_{0.27}CuO_4$ [25] and $La_{2-X-Y}R_XSr_YCuO_4$ ($R$ = Sm, Eu, Gd) [14, 15].

In all high-$T_C$ materials the charge carriers are extrinsic, i.e., superconductivity involves holes or defect electrons and atomistic simulation techniques allow an estimation of the formation energies of these defects. Within the framework of an ionic model, valence band holes are described in localised terms as $Cu^{3+}$ ($h_{Cu}$) or $O^-$ ($h_O$) and defect electrons as $Cu^+$ ($e_{Cu}$). The formation energy of these defects involves a contribution from the ionisation potential/electron affinity of the appropriate ion in addition to a lattice energy term (including the effects of relaxation) and a band contribution, in the case of delocalised carriers (large polarons).

Defect energies in which both cores and shells are relaxed are often referred to as "thermal" energies in that they correspond to lattices in thermal equilibrium. The corresponding energies in which only the shells are allowed to relax are referred to as "optical" energies. In the present context of electronic defects in oxides, the difference between "optical" and "thermal" energies is important because it permits a quantitative distinction to be made between descriptions of free carriers (either holes or electrons) in the large (${}^lh_{Cu}$, ${}^lh_O$, ${}^le_{Cu}$) and small (${}^sh_{Cu}$, ${}^sh_O$, ${}^se_{Cu}$) polaron limits [26]. Full details of all the relevant terms have been given in our earlier work [2–4]; here for 5-coordinate Cu we have used the same band contributions as for 4-coordinate Cu [3]. As mentioned previously [4] the concept of the polaron involves the coupling of the free carrier to the oscillating electric field of a vibrating polar lattice and so is essentially dynamic in nature. The justification of static calculations is that a static description (the zero-frequency limit of the dynamic case) contains all the essential physics of the problem [27, 28].

In the binary oxides formed by the elements adjacent to the Cu in the Periodic Table, holes are essentially O $2p$ in character in ZnO and $3d$ in character in the transition metal oxides FeO, CoO and NiO. It might be anticipated, therefore, that holes in Cu oxides are of mixed character.

Table 2 collects together the calculated hole and defect electron formation energies for a large number of cuprates from the present and previous work [2–4, 12, 17]. The values listed are for large or small polarons according to whichever is lower. Figure 2 shows graphically the variation of these quantities with copper coordination for a large number of these systems.

Our estimates of hole energies, and from these the essential character of the lowest energy holes, indicate a strong dependence on crystal structure and/or Cu coordination. Furthermore, we find a greater variation with local environment for Cu holes (and defect electrons) than O holes. In $La_2CuO_4$ and $Bi_2Sr_2CuO_6$, in which the Cu coordination is 6-fold, calculations favour holes with Cu $3d$ character; for systems containing 4-fold coordinated Cu, on the other hand, whether in $CuO_2$ planes, as in $Nd_2CuO_4$ or $Y_2CuO_4$, or in $CuO_2$ chains, as in $Ca_2CuO_3$ or $Sr_2CuO_3$, O $2p$ holes are found to be lower in energy. In $YBa_2Cu_3O_6$ and $LaNdCuO_4$ containing Cu in 5-fold coordination, Cu holes appear to be favoured, although the difference in energy between Cu and O holes is smaller than in $La_2CuO_4$. The values for $La_2CuO_4$ in the hypothetical $T^*$ and $T'$ structures are entirely in keeping with those of $LaNdCuO_4$ and $Nd_2CuO_4$ respectively which suggest that Cu-coordination is more important that the

**Table 2** Estimated hole and defect formation energies for a wide range of ternary and quaternary cuprates (eV). The notation used is such that, for example, ${}^{l}h_{\mathrm{Cu}}$ denotes a *l*arge polaron *h*ole on *Cu*. The values given are for small or large polarons, whichever is the lower. For $YBa_2Cu_3O_6$ the values given refer to holes and defect electrons in the $CuO_2$ planes.

| *Compound* | *Lowest energy holes* | | | | *Defect electrons* | |
|---|---|---|---|---|---|---|
| $La_2CuO_4$ ($T$) | ${}^{l}h_{\mathrm{Cu}}$ | 1.5 | ${}^{l}h_{\mathrm{O}}$ | 3.0 | ${}^{s}e_{\mathrm{Cu}}$ | 2.7 |
| ($La_2CuO_4$ ($T^*$) | ${}^{s}h_{\mathrm{Cu}}$ | 2.5 | ${}^{l}h_{\mathrm{O}}$ | 3.1 | ${}^{s}e_{\mathrm{Cu}}$ | 0.8)# |
| ($La_2CuO_4$ ($T'$) | ${}^{s}h_{\mathrm{O}}$ | 3.2 | ${}^{s}h_{\mathrm{Cu}}$ | 3.8 | ${}^{s}e_{\mathrm{Cu}}$ | −2.4)# |
| $LaNdCuO_4$ ($T^*$) | ${}^{s}h_{\mathrm{Cu}}$ | 2.2 | ${}^{l}h_{\mathrm{O}}$ | 3.0 | ${}^{s}e_{\mathrm{Cu}}$ | 0.5 |
| $Nd_2CuO_4$ | ${}^{l}h_{\mathrm{O}}$ | 3.1 | ${}^{s}h_{\mathrm{Cu}}$ | 4.2 | ${}^{s}e_{\mathrm{Cu}}$ | −0.9 |
| $Y_2CuO_4$ | ${}^{l}h_{\mathrm{O}}$ | 3.8 | ${}^{l}h_{\mathrm{Cu}}$ | 4.3 | ${}^{s}e_{\mathrm{Cu}}$ | −0.4 |
| $Ca_2CuO_3$ | ${}^{l}h_{\mathrm{O}}$ | 3.3 | ${}^{l}h_{\mathrm{Cu}}$ | 4.2 | ${}^{s}e_{\mathrm{Cu}}$ | −0.7 |
| $Sr_2CuO_3$ | ${}^{l}h_{\mathrm{O}}$ | 2.4 | ${}^{l}h_{\mathrm{Cu}}$ | 3.9 | ${}^{s}e_{\mathrm{Cu}}$ | −0.8 |
| $Al_2CuO_4$ | ${}^{l}h_{\mathrm{Cu}}$ | 5.8 | ${}^{l}h_{\mathrm{O}}$ | 6.4 | ${}^{l}e_{\mathrm{Cu}}$ | −0.6 |
| $Bi_2Sr_2CuO_6$ | ${}^{l}h_{\mathrm{Cu}}$ | 1.4 | ${}^{l}h_{\mathrm{O}}$ | 2.2 | ${}^{s}e_{\mathrm{Cu}}$ | 2.7 |
| $YBa_2Cu_3O_6$ | ${}^{s}h_{\mathrm{Cu(2)}}$ | 2.6 | ${}^{l}h_{\mathrm{O(2)}}$ | 3.3 | ${}^{s}e_{\mathrm{Cu(2)}}$ | 1.8 |

# Phases not observed experimentally.

size of the lanthanide ion in determining the energies of electronic defects. Finally, the hole energies for the non-superconductor $Al_2CuO_4$ [3], which possesses the spinel structure (no $CuO_2$ planes), in which the Cu is tetrahedrally coordinated to O, are much larger than those for any of the other systems.

It is important to emphasise that the relatively crude estimates of hole (and defect electron) energies which are obtained from atomistic simulations cannot serve the role of electronic structure calculations on these materials. The differences in the calculated energies of Cu and O holes are small bearing in mind the approximations made in the calculations, which suggests that holes in all these materials are of mixed character or that both types of hole might coexist. Nevertheless we find clear variations with Cu coordination, which suggest an increase in the O character of holes with decreasing Cu coordination.

It is evident from Table 2 and Figure 2 that the hole formation energies in $La_2CuO_4$ and $Bi_2Sr_2CuO_6$ (6-coordinate Cu) is considerably smaller than in any of the other systems. Conversely the formation energies of defect electrons appear to be lowest for systems in which the Cu is 4-coordinate. This has very important consequences for the associated redox energies of these compounds. Since the charge carriers in high-$T_C$ oxides are extrinsically controlled, superconductivity is intimately connected with the energetics of the redox reactions which control the non-stoichiometry in the presence of oxygen and the equilibrium between lattice and electronic defects. Using the usual Kroger–Vink notation the most important of these reactions [4] are:

$$\tfrac{1}{2}\mathrm{O}_2(g) = \mathrm{O}_i'' + 2h^{\cdot} \tag{1}$$

$$2M_M^X + \mathrm{Cu}_{\mathrm{Cu}}^X + 2\mathrm{O}_2(g) = 2V_M''' + V_{\mathrm{Cu}}'' + 8h^{\cdot} + \mathrm{M}_2\mathrm{CuO}_4 \tag{2}$$

$$\mathrm{O}_0^X = \tfrac{1}{2}\mathrm{O}_2(g) + V_0^{\cdot\cdot} + 2e' \tag{3}$$

$$V_0^{\cdot\cdot} + \tfrac{1}{2}\mathrm{O}_2(g) = \mathrm{O}_0^X + 2h^{\cdot} \tag{4}$$

$$\mathrm{O}_i'' = \tfrac{1}{2}\mathrm{O}_2(g) + 2e' \tag{5}$$

$$2V_M''' + V_{\mathrm{Cu}}'' + 4\mathrm{O}_0^X = 2\mathrm{O}_2(g) + 8e' \tag{6}$$

with associated energies $E_1$–$E_6$ respectively. The calculated values of these for

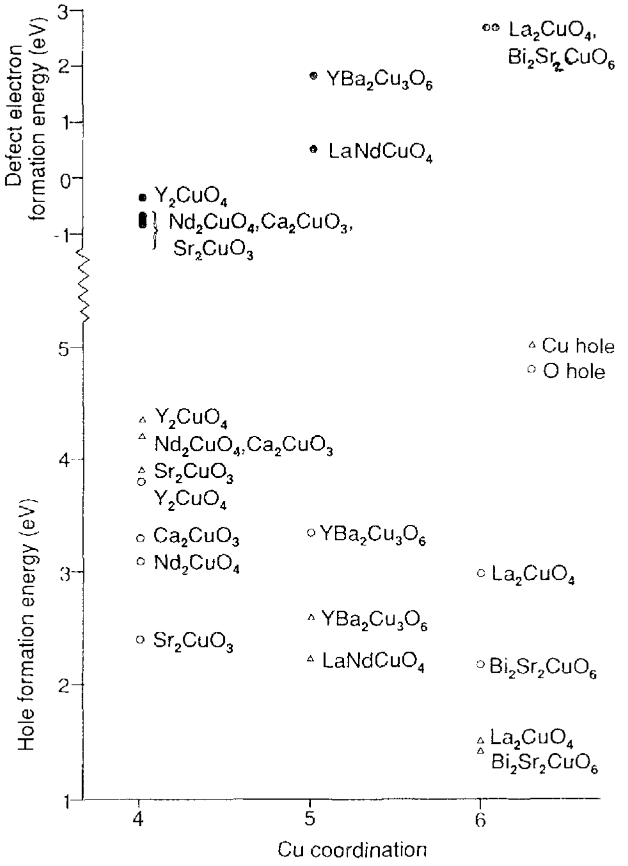

**Figure 2** Calculated hole and defect electron formation energies (eV) for a range of cuprates (containing $CuO_2$ planes and/or chains) versus the copper coordination to oxygen.

$La_2CuO_4$, $LaNdCuO_4$, $Nd_2CuO_4$ and $YBa_2Cu_3O_6$ are listed in Table 3. The figures in parentheses are estimates of $E_4$–$E_6$ at 1000 K (approximately the synthesis temperature of these materials). These have been calculated allowing for the significant contribution to the total free energies of these reactions for the entropic contribution of $O_2(g)$ and assuming that all the relevant defect energies are independent of temperature.

A puzzling feature of high-$T_C$ oxides, for which no fundamental explanation in terms of electronic structure considerations appears to have been forthcoming, is why $La_2CuO_4$ apparently leads only to "hole" superconductors and $Nd_2CuO_4$ only to "electron" superconductors, despite the similarity in their crystal structures. However, a tentative explanation lies in the nature of their redox equilibria. Substitution of $RE^{3+}$ ($RE$ = La, Nd) by divalent ions in principle leads to charge compensation by either oxygen vacancies or holes, and substitution by 4+ ions to cation vacancies, oxygen interstitials or defect electrons. The criteria for electronic compensation by

**Table 3** Calculated redox energies (eV) for tetragonal $La_2CuO_4$, $LaNdCuO_4$, $Nd_2CuO_4$, $Y_2CuO_4$ and $YBa_2Cu_3O_6$. The details of reactions 1–6 are given in the text. The energies all refer to 0 K except for those in parentheses which relate to 1000 K.

| *Energy* | $La_2CuO_4$ | $LaNdCuO_4$ | $Nd_2CuO_4$ | $Y_2CuO_4$ | $YBa_2Cu_3O_6$[*] |
|---|---|---|---|---|---|
| $E_1$[†] | 0.7 | 1.4 | 3.1 | 5.4 | −0.5[#] |
| $E_2$ | 4.5 | 9.5 | 18.6 | 23.9 | 13.5 |
| $E_3$ | 9.9 | 6.3 | 4.2 | 4.9 | 8.9 |
| $E_4$ | −1.5 (−0.3) | −0.9 (0.3) | 0.2 (1.4) | 1.9 (3.1) | −0.1 (1.1) |
| $E_5$ | 7.7 (6.5) | 4.0 (2.8) | 1.1 (−0.1) | 1.4 (0.2) | 9.2 (8.0) |
| $E_6$ | 29.1 (24.3) | 12.2 (7.3) | −1.0 (−5.8) | 3.3 (−1.5) | 39.3 (34.5) |

[*] For $YBa_2Cu_3O_6$ the energies listed refer to reactions analogous to those for the $M_2CuO_4$ systems [17].

[†] Calculated lowest energy interstitial oxygen positions are, with reference to Figure 1, (0, 0.5, ≈0.25) ($La_2CuO_4$), (0, 0.5, ≈0.75) ($LaNdCuO_4$), (0, 0, ≈0.25) ($Nd_2CuO_4$, $Y_2CuO_4$), (0, 0.5, 0) ($YBa_2Cu_3O_6$).

[#] In this case $E_1$ is the value for the formation of a basal plane interstitial oxide ion bound to 2 Cu(1) holes. See Section 6.

either holes or defect electrons are determined by the values of $E_4$–$E_6$ and hence to the relative formation energies of lattice and electronic defects.

It is clear from Table 3 that oxygen vacancies in $La_2CuO_4$ are unstable with respect to the formation of holes in oxygen deficient $La_2CuO_4$, whereas cation vacancies are calculated to be stable with respect to electrons in the corresponding cation deficient systems. From this it can be shown that the solution of CaO, SrO and BaO in $La_2CuO_4$ leads to systems of the type $La_{2-X}M_XCuO_4$, in which the impurity defects $M'_{La}$ are compensated by holes, rather than $La_{2-X}M_XCuO_{4-X/2}$ or $La_2Cu_{1-X}M_XO_4$. On the other hand, holes are unstable with respect to oxygen vacancies in oxygen-deficient $Nd_2CuO_4$ and electrons stable with respect to cation vacancies in cation-deficient material so that divalent impurities leads to systems of the type $Nd_{2-X}M_XCuO_{4-X/2}$ and 4-valent impurities to $Nd_{2-X}M_XCuO_4$ above 1000 K. In summary, $La_2CuO_4$ is readily oxidised, $Nd_2CuO_4$ readily reduced.

The behaviour of $LaNdCuO_4$ is intermediate between that of $La_2CuO_4$ and $Nd_2CuO_4$. Holes are stable with respect to oxygen vacancies at low temperatures and defect electrons unstable with respect to lattice defects; in this the $T^*$ structure is more similar to $T$ than to $T'$ which, as is mentioned at the beginning of this section, rationalises why the $T^*$ structure only superconducts when doped $p$-type. The increase in $E_4$ in the series $La_2CuO_4$-$LaNdCuO_4$-$Nd_2CuO_4$ also explains why oxygen treatment is needed for bulk superconductivity in the $T^*$ phase [29]. In summary, the calculated redox energies show in a striking way how, solely on stability grounds, $La_2CuO_4$ and $LaNdCuO_4$ (6- and 5-coordinate Cu) would be expected to lead to hole superconductivity and $Nd_2CuO_4$ (4-coordinate Cu) to high-$T_C$ electron superconductivity.

## 5 $Y_2CuO_4$

$Y_2CuO_4$ has been prepared recently by Okada *et al.* [16] at high pressure and found to possess the $Nd_2CuO_4$ structure (4-coordinate Cu) as predicted somewhat earlier by Allan *et al.* [3]. However, since $Y^{3+}$ is considerably smaller than $Nd^{3+}$ ($r(Nd^{3+}) \approx 1.16$ Å, $r(Y^{3+}) \approx 1.015$ Å [16]) it would seem to be of interest to compare the predicted defect chemistry of the two materials.

The calculated formation energies of electronic defects and the redox energies given in Tables 2 and 3 respectively show that the two compounds generally exhibit similar behaviour. Hole and defect electron energies are found to be larger in $Y_2CuO_4$ than in $Nd_2CuO_4$; however in both materials holes are predicted to be unstable with respect to the formation of oxygen vacancies at all temperatures, with $E_4$ larger for $Y_2CuO_4$ than $Nd_2CuO_4$. $E_6$ is also predicted to be considerably greater for $Y_2CuO_4$ than for $Nd_2CuO_4$. In $Y_2CuO_4$ defect electrons are predicted to be unstable with respect to cation vacancies and oxygen interstitials at 0 K. allowing for entropy effects at higher temperatures defect electrons are found to be just stable with respect to lattice defects at temperatures greater than 1000 K. Since the estimates of the redox energies involve contributions from a large number of terms, the stability of defect electrons at elevated temperatures remains unclear.

Our calculations therefore predict that $Y_2CuO_4$ will not lead to hole superconductors whilst the possibility of electron superconductivity remains open. The calculated solution energies for substitution of $Y^{3+}$ by $Ce^{4+}$, $Th^{4+}$ and $Zr^{4+}$ are considerably higher than the corresponding values for $Nd_2CuO_4$, so whether the critical carrier concentration can be achieved by doping is also uncertain. In view of the smaller size of $Y^{3+}$, doping with a smaller 4+ cation might be considered. As yet there appear to be no reports of the properties of doped $Y_2CuO_4$, including the absence or presence of superconductivity, but clearly experimental studies would be very valuable. Thus, at present, the question as to whether all $M_2CuO_4$ systems with the $Nd_2CuO_4$ structure might lead to electron superconductors remains unresolved.

## 6 $YBa_2Cu_3O_6$

As our last example we consider the calculated defect chemistry of $YBa_2Cu_3O_6$, which can be regarded as the "parent" oxide of $YBa_2Cu_3O_{7-X}$, the first system found to possess a $T_C$ ($\approx 90$ K) at liquid nitrogen temperatures [30]. With reference to Figure 1, $YBa_2Cu_3O_7$ can be considered formally as derived from semiconducting $YBa_2Cu_3O_6$ by the doping of the vacant O(4) site by oxygen. As noted previously, in the context of the present paper $YBa_2Cu_3O_6$ possesses both 5-coordinated Cu (*cf.* the $T^*$ structure of $LaNdCuO_4$) and 2-coordinated Cu, which electronic structure [19] and our atomistic simulation studies indicate are in different oxidation states – the former Cu(II), the latter Cu(I).

Charge carriers in $YBa_2Cu_3O_{6+X}$ are formed not by aliovalent substitution of $Y^{3+}$ (*cf.* $La_{2-X}Sr_XCuO_4$ and $Nd_{2-X}Ce_XCuO_4$) but by oxygen incorporation (*cf.* $La_2CuO_{4+X}$). The variation of $T_C$ with oxygen content $X$ [18, 31] shown in Figure 3 is of particular interest and invites theoretical explanation. There is considerable variation between samples prepared by different techniques, and in particular, between samples are prepared by quenching from high temperature and those prepared by low temperature reduction of $YBa_2Cu_3O_7$. However despite these differences it is generally accepted that high $T_C$ behaviour does not occur for $X < \approx 0.3$. In contrast, superconductivity has been observed at $\approx 50$ K in $Y_{1-Z}Ca_ZBa_2Cu_3O_6$ [32, 33], in which the charge carriers are introduced by the substitution of $Y^{3+}$ by $Ca^{2+}$, as in $La_{2-X}Ca_XCuO_4$. Figure 3 also shows the variation of $T_C$ with $X$ for $Y_{1-Z}Ca_ZBa_2Cu_3O_{6+X}$. 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.* [34], 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 $X$.

Calculated hole formation energies in $YBa_2Cu_3O_6$ (Table 1 – see also Reference 17) shows that the lowest energy free carrier to be a Cu hole in the (super)conducting $CuO_2$ planes. Oxygen holes in the $CuO_2$ planes are predicted to have similar energies

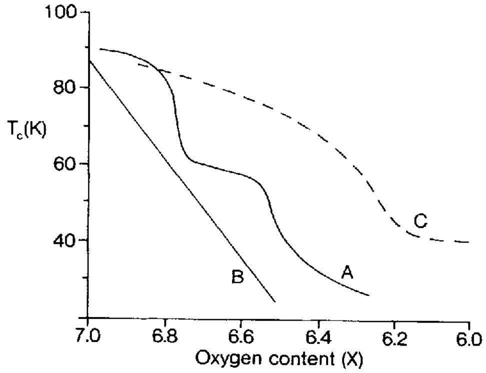

**Figure 3** Schematic variation of $T_C$ with oxygen content $X$ for $YBa_2Cu_3O_{6+X}$ samples prepared by different techniques (A [18], B [31]) and for $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{6+X}$ (C [33]).

(*cf.* the comparable calculated hole energies of compounds with the $T^*$ structure), as are holes at the O(1) apical position ($\approx 2.8$ eV), allowing for the uncertainties associated with terms that contribute to the total energy of formation. As with $La_2CuO_4$, the calculated redox energies $E_1$–$E_6$ (Table 3) indicate that holes are stable with respect to the formation of oxygen vacancies and defect electrons unstable with respect to cation vacancies and oxygen interstitials.

The calculated energy, $E_1$ ($\approx -0.5$ eV), for the incorporation of oxygen:

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

is lower than the corresponding value for $La_2CuO_4$ and compares with the experimental value of $\sim -1.0$ eV [35, 36]. The lowest energy interstitial position is found to be the O(4) site in the basal plane in agreement with experiment. This 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 much greater in energy. This strong interstitial-hole association is not found in $La_2CuO_4$ [4], where the interstitial oxygen is in a different location away from the $CuO_2$ planes (at (0, 0.5, $\approx$0.25) and is stabilised by four nearest-neighbour $La^{3+}$ cations.

Our calculations suggest that the absence of superconductivity in the $YBa_2Cu_3O_{6+X}$ system for $X < \approx 0.3$ can be accounted for by the predicted formation of holes which are trapped by negatively-charged oxygen interstitials at the O(4) position in the basal plane, rather than free holes in the $CuO_2$ planes, in broad agreement with Goodenough's view [37]. In $Y_{1-Z}Ca_ZBa_2Cu_3O_6$, on the other hand, the basal plane is devoid of both lattice and interstitial oxygen, so that holes introduced by Ca will be located, at least in part, in the $CuO_2$ planes leading to superconductivity. This would seem to be a plausible explanation for high $T_C$ behaviour in Ca-doped materials with oxygen content less than $\approx 6.3$ [32, 33]. As in $La_2CuO_4$ [2], calculated association energies between the Ca dopant and $CuO_2$ plane holes are very small, which contrasts markedly with the strong association of basal plane holes to added oxygen. Thus, the occurrence of two types of Cu atoms has very important implications for the superconducting behaviour of Y–Ba–Cu–O ceramics.

## 7 CONCLUSIONS

In this paper we have considered the calculated defect chemistry of a large number of complex cuprates containing Cu atoms in various coordinations, and have attempted to relate the differences in the defect properties to the high temperature superconducting behaviour. A comparison of calculated hole energies in systems containing 6-, 5- and 4-coordinated Cu suggests an increase in O $2p$ character with decreasing Cu coordination. The variations in hole and defect electron formation energies explain why $La_2CuO_4$ is easily oxidised and $Nd_2CuO_4$ readily reduced and consequently why materials with the $T$ and $T^*$ structures are hole superconductors, while $T'$ compounds exhibit $n$-type superconductivity. In this context it is of interest to consider $Ca_{0.86}Sr_{0.14}CuO_2$ [38], the $n = \infty$ parent of the $A_2B_2Ca_{n-1}Cu_nO_{4+2n}$ ($A$ = Bi, Tl; $B$ = Sr, Ba) superconductors. This contains 4-fold coordinated Cu in $CuO_2$ planes (as in the $T'$ structure adopted by $Nd_2CuO_4$) separated only by $Ca^{2+}$ ions and is itself not superconducting when doped $p$-type; $n$-type superconductivity has recently been reported in system $Sr_{1-X}Nd_XCuO_2$ [39], which is a lower valent analogue of $Nd_{2-X}Ce_XCuO_4$. Atomistic simulation studies of these two systems are currently in progress. We have also considered the defect properties of $Y_2CuO_4$. Experimental resolution as to whether this material can be made superconducting is still awaited.

Finally, in $YBa_2Cu_3O_6$, which contains Cu in both 5-fold (Cu(II)) and 2-fold (Cu(I)) coordination, we have drawn attention to the necessity to oxidise the 5-fold site for superconductivity, thereby explaining the observed difference in behaviour between $YBa_2Cu_3O_{6+X}$ and $Y_{1-Z}Ca_ZBa_2Cu_3O_{6+X}$ for $X < \approx 0.3$. In the form the incorporation of $O^{2-}$ ions at the vacant O(4) sites localizes the accompanying holes in the basal plane, whereas substitution of Y by Ca leads to oxidation of, i.e., hole generation in, the conducting $CuO_2$ planes.

We reiterate that our calculations of the energies of the electronic defects in these materials cannot serve the role of appropriate "*ab initio*" electronic structure studies: they do, however, highlight the importance of the lattice contribution in determining the defect properties of these materials. Furthermore they appear to illustrate in a striking way qualitative differences between systems containing Cu in different environments. In summary, atomistic lattice simulations are able to calculate many important properties of high-$T_C$ oxides that are clearly relevant to their superconducting behaviour.

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