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relationship to La_2CuO_4 and high-T_c superconductivity

Calculated crystal and defect properties of ternary cuprates M_2CuO_3 (M ≡ Ca, Sr): relationship to La_2CuO_4 and high-T_c superconductivity

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Abstract. Attention is drawn to the requisite dimensionality of the superconducting networks in high-T_c ternary and quaternary cuprates. Calculations are reported of the lattice and defect properties of Ca_2CuO_3 and Sr_2CuO_3 compared with those of La_2CuO_4. The former consist of one-dimensional CuO_2 chains, and the latter of two-dimensional CuO_2 planes; both lead to calculated phonon densities of states which are similar in the 10 meV region. Different defect structures are calculated for the two types of material: La vacancies and holes in La_2CuO_4, and O interstitials and holes in Ca_2CuO_3 and Sr_2CuO_3. In both cases, however, the putative conducting networks are free of Cu and O vacancies. Li is predicted to substitute for both cation sublattices in Ca_2CuO_3 and Sr_2CuO_3, but Na solely for the alkaline-earth ions with the creation of holes. These are predicted to be largely O 2p band, as in Nd_2CuO_4, unlike La_2CuO_4, for which Cu 3d band holes were found to be lowest in energy.

1. Introduction

The discovery of high-T_c superconductivity in ceramic oxides has raised a number of questions related to the electronic structure and density of states (Mattheiss 1987, Yu *et al* 1987, Bullett and Dawson 1987), spin configurations (Vaknin *et al* 1987, Guo *et al* 1988), charge states (Liang 1987, Wilson 1987), coupling mechanisms (Anderson 1987, Varma *et al* 1987, Emery 1987, Ruvalds 1987), the nature of the lattice and electronic defects (Shafer *et al* 1987, Alp *et al* 1987, Allan and Mackrodt 1988a, b, c), oxidation–reduction characteristics (Shafer *et al* 1987, Johnston *et al* 1987, Allan and Mackrodt 1988a, b, c) and the role of impurities (Hasegawa *et al* 1987, Allan and Mackrodt 1988a, b, c). A fundamental structural issue which, apparently, is unresolved at the time of writing is whether superconductivity in these materials is essentially two dimensional or whether high-T_c behaviour can be exhibited by one-dimensional networks. La_2CuO_4-based systems, with T_c-values in the region of about 20–40 K, consist solely of two-dimensional 'CuO_2' planes, shown hatched in figure 1(*a*), and in these and similar materials (Allan and Mackrodt 1988a, b, c) it has been shown that superconductivity is two-dimensional in the *a–b* plane (Shamoto *et al* 1987). Likewise the superconducting

phases in the new Tl–Ca–Ba–Cu–O system reported recently by Sheng and Herman (1988), with T_c-values above 100 K, consist solely of 'CuO$_2$' planes, so that it seems reasonable to conclude that superconductivity in these materials is also two dimensional. YBa$_2$Cu$_3$O$_{6.5+x}$, on the contrary, and materials with a similar structure, contain both two-dimensional planes (hatched) and one-dimensional chains (shaded), shown in figure 1(b), and while there is a growing view that superconductivity is also two-dimensional in these materials, the role of the one-dimensional chains being essentially that of controlling the O stoichiometry, this has not been proven with certainty. An issue
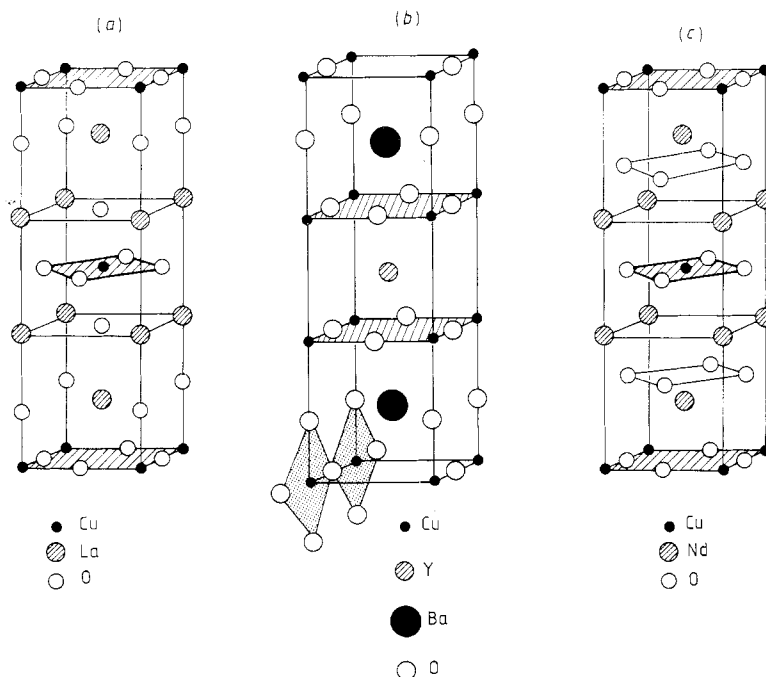

Figure 1. The crystal structures of (a) La$_2$CuO$_4$, (b) YBa$_2$Cu$_3$O$_{6.5}$ and (c) Nd$_2$CuO$_4$.

as fundamental as this needs to be resolved, if high-T_c oxides are to be thoroughly understood, and the most direct way would be to examine purely one-dimensional analogues of La$_2$CuO$_4$ or YBa$_2$Cu$_3$O$_{6.5+x}$. Accordingly, the present paper suggests ternary cuprates of this type and reports the calculated lattice and defect properties of these materials compared with those of La$_2$CuO$_4$.

The ternary cuprates that we investigate here are Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$, the observed structures of which have been reported previously (Teske and Muller-Buschbaum 1969, 1970). With regard to high-T_c superconductivity the relationship to La$_2$CuO$_4$ which we have in mind is essentially twofold. The first is structural and is seen by comparing figures 1(a) and 2(a); La$_2$CuO$_4$ consists of CuO$_2$ planes (hatched) in which the Cu is (near) square four coordinated (in addition to the two long Cu–O bonds in the c direction), whereas Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$ consist of four coordinated Cu in the form
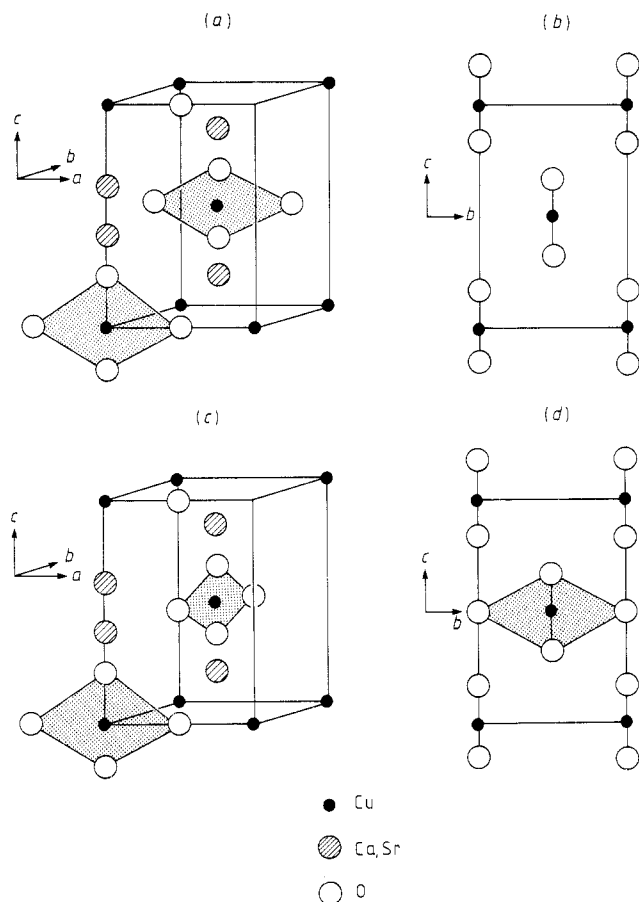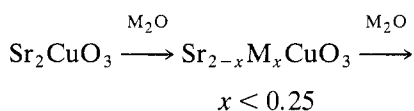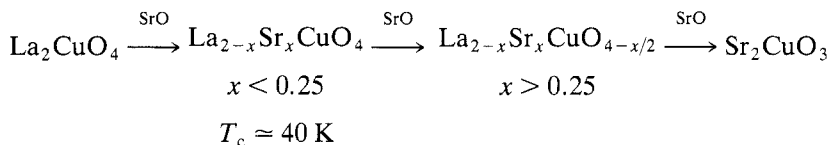
Figure 2. The crystal structures of (*a*), (*c*) Ca_2CuO_3 and (*b*), (*d*) Sr_2CuO_3: (*a*), (*b*) the orthorhombic structures; (*c*), (*d*) the tetragonal structures.

of CuO_2 chains (shaded). The second is compositional and is best illustrated by the following series of substitution reactions:

$$La_2CuO_4 \xrightarrow{\text{SrO}} La_{2-x}Sr_xCuO_4 \xrightarrow{\text{SrO}} La_{2-x}Sr_xCuO_{4-x/2} \xrightarrow{\text{SrO}} Sr_2CuO_3$$

$$x < 0.25 \qquad\qquad x > 0.25$$

$$T_c \simeq 40\ K$$

$$Sr_2CuO_3 \xrightarrow{\text{M}_2\text{O}} Sr_{2-x}M_xCuO_3 \xrightarrow{\text{M}_2\text{O}}$$

$$x < 0.25$$

The speculation, then, is whether $Sr_{2-x}M_xCuO_3$ (M $\equiv$ Li, Na, K) might exhibit similar high-T_c behaviour to that of La_2CuO_4. Previously it has been argued (Allan and Mackrodt 1988a, b, c) that, since the density of hole states (Shafer *et al* 1987), the location and concentration of O vacancies (Tarascon *et al* 1987) and the nature and level of

impurities (Hasegawa *et al* 1987) have been shown to play a crucial role in determining T_c in La_2CuO_4, a general appraisal of the lattice and defect structure might reveal valuable clues as to some of the necessary conditions for high-T_c behaviour.

Following this line of approach, a range of ternary cuprates of the type M_2CuO_4 (M $\equiv$ Pr, Nd, Y, Al) have been examined theoretically in an attempt to understand why, apparently, La_2CuO_4 is alone in leading to superconducting materials (Allan and Mackrodt 1988b, c). Here we extend this approach to Ca_2CuO_3 and Sr_2CuO_3 and compare features of the lattice and defect structure that seem to be most related to high-T_c superconductivity (Mackrodt 1989) with those of La_2CuO_4 and also Nd_2CuO_4, which, it was suggested recently, might exhibit high-T_c behaviour (Allan and Mackrodt 1988c).

2. Theoretical methods

The theoretical methods used here are identical with those used in recent studies of superconducting ceramics (Allan and Mackrodt 1988a, b, c) and broadly similar to those used previously for a wide variety of ceramic oxides (Mackrodt 1984). The calculations are formulated within the framework of an ionic model and are based on two-body electron-gas potentials (Mackrodt and Stewart 1979) and the shell approach to ionic polarisation (Dick and Overhauser 1958). The potentials for M_2CuO_3 (M $\equiv$ Mg, Ca, Sr and Ba) are exactly those for CuO and MgO, CaO, SrO and BaO, without any modification to the shell parameters (Allan *et al* 1988). Furthermore, a single $O^{2-}-O^{2-}$ potential has been used for the entire range of oxides. As before, the treatment of the defective lattice follows the two-region strategy introduced by Lidiard and Norgett (1972) and described in full elsewhere (Catlow and Mackrodt 1982).

3. Lattice properties

3.1. Crystal structure

The crystal structures of La_2CuO_4 and Nd_2CuO_4 are shown in figure 1 and those of Ca_2CuO_3 and Sr_2CuO_3 in figures 2(a) and 2(b). The former contain the putative CuO_2 conducting planes (hatched), and the latter the corresponding chain structure (dotted). An important similarity between Ca_2CuO_3, Sr_2CuO_3 and Nd_2CuO_4, however, is that Cu is planar four-coordinated by O in these materials, whereas it is octahedrally coordinated in La_2CuO_4. The calculated lattice parameters are given in table 1. For La_2CuO_4 they differ from the observed values by less than 1% and those of Nd_2CuO_4, Ca_2CuO_3 and Sr_2CuO_3 by less than 2%. In addition, bond lengths in Ca_2CuO_3 and Sr_2CuO_3 not directly related to the lattice constants, namely the Cu–O and M–O bonds in the c direction are also within 1% of the observed values, thus vindicating our use of the potentials for the binary oxides unchanged. We have also found tetragonal structures for Ca_2CuO_3 and Sr_2CuO_3 shown in figures 2(c) and 2(d), in which there are CuO_2 chains in both the a and b directions. The corresponding lattice parameters are close to those of the orthorhombic structures and the calculated lattice energies 0.4 eV and 0.25 eV higher. As discussed later, these higher-energy structures might be involved in the intrinsic defect structures. For completeness, we have also calculated the crystal structures of the hypothetical Mg and Ba analogues; these are given in table 2.

Table 1. Calculated crystal structures and lattice energies of La_2CuO_4, Nd_2CuO_4, Ca_2CuO_3 and Sr_2CuO_3. For La_2CuO_4 the a- and b-values are divided by $2^{1/2}$ for comparison with those of the other systems. The experimental values in parentheses are taken from the following references: La_2CuO_4 from Grande *et al* (1977), Nd_2CuO_4 from Muller-Buschbaum and Wollschlager (1975), Ca_2CuO_3 from Teske and Muller-Buschbaum (1970) and Sr_2CuO_3 from Teske and Muller-Buschbaum (1969). M ≡ Ca, Sr.

Parameter (units)	La_2CuO_4	Nd_2CuO_4	Ca_2CuO_3	Sr_2CuO_3
a (Å)	3.837	3.898	3.688	3.892
	(3.823)	(3.945)	(3.77_9)	(3.91)
b (Å)	3.784	—	3.256	3.474
	(3.797)	—	(3.25_9)	(3.48)
c (Å)	12.994	11.985	12.553	13.067
	(13.15)	(12.171)	(12.23_9)	(12.68_8)
Cu–O (c)	—	—	1.979	1.949
			(1.96)	(1.96)
M–O	—	—	2.338	2.595
			(2.33)	(2.51)
W_L (eV)	−172.71	−189.64	−115.60	−111.04

Table 2. Calculated crystal structures and lattice energies of Mg_2CuO_3 and Ba_2CuO_3. M ≡ Mg, Ba.

Parameter (units)	Mg_2CuO_3	Ba_2CuO_3
a (Å)	3.446	3.686
b (Å)	2.880	4.064
c (Å)	11.778	14.015
Cu–O (c)	1.938	2.399
M–O	1.939	2.391
W_L (eV)	−124.12	−105.74

3.2. Thermodynamic stability

The series M_2CuO_3 (M ≡ Mg, Ca, Sr and Ba) is unusual in that both end members, apparently, do not exist and hence might reasonably be assumed to be thermo-dynamically unstable. As a further test of our potentials, therefore, we have calculated the energies of the formation reaction

$$2MO + CuO \rightleftharpoons M_2CuO_3 \quad (M \equiv Mg, Ca, Sr \text{ and } Ba).$$
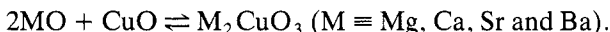
Relative to that of Ca_2CuO_3 the formation energies of Mg_2CuO_3, Sr_2CuO_3 and Ba_2CuO_3 are 1.04 eV, −0.05 eV and 0.97 eV, respectively. Thus we predict Ca_2CuO_3 and Sr_2CuO_3 to be thermodynamically more stable with respect to the parent oxides than are Mg_2CuO_3 and Ba_2CuO_3 by approximately 1 eV, which is in qualitative agreement with the known compounds.

3.3. Phonon density of states

It has been argued previously (Allan and Mackrodt 1988a, b, c) that, while coupling mechanisms in high-T_c oxides remain the subject of controversy, there is both theoretical
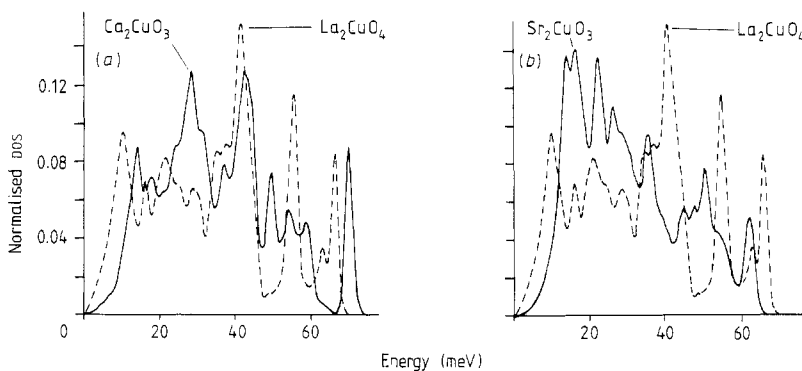
Figure 3. A comparison of the calculated phonon densities of states of La_2CuO_4 and Ca_2CuO_3 and Sr_2CuO_3.

(Weber 1987, Bardeen 1988) and experimental (Ramirez *et al* 1987) evidence that phonon coupling makes a major contribution in $La_{2-x}Sr_xCuO_4$. For this material, it has been shown (Weber 1987) that coupling is associated with a strong peak in the phonon density of states at about 10 meV, corresponding to the 'in-plane' breathing mode of the four equatorial O atoms in the CuO_2 plane. Neutron scattering data for the undoped material (Balakrishnan *et al* 1987) show a nearly identical peak at about 10 meV, which, it has been suggested (Weber 1987, Ramirez *et al* 1987), is renormalised in the superconducting phases. Figure 3 shows the calculated phonon densities of states of Ca_2CuO_3 and Sr_2CuO_3 compared with that of orthorhombic La_2CuO_4. In both cases there is a strong peak in the 10 meV region but shifted to higher energy by 3–4 meV. A similar shift of a few millielectronvolts has been calculated for Nd_2CuO_4 (Allan and Mackrodt 1988c) and also found in the observed phonon density of states of $YBa_2Cu_3O_7$ (Rhyne *et al* 1987). We conclude from this that a strong phonon peak at about 15 meV is characteristic of structures with Cu planar four coordinated by O in either two-dimensional planes or one-dimensional chains. A further similarity with $YBa_2Cu_3O_7$ is the presence of a strong peak at about 25 meV (Rhyne *et al* 1987).

4. Defect structure

It has been recognised for some time that point defects play a crucial role in controlling T_c in ternary cuprates (Welch *et al* 1987, Phillips 1987, Shafer *et al* 1987, Johnston *et al* 1987). In the present section, therefore, we compare the calculated defect structures of La_2CuO_4 and Nd_2CuO_4 with those of Ca_2CuO_3 and Sr_2CuO_3. Schottky defects have been calculated to predominate the lattice disorder in La_2CuO_4 and Nd_2CuO_4 (Allan and Mackrodt 1988a, b, c) with formation energies of 2.2 eV and 2.7 eV per defect, respectively. For Ca_2CuO_3 and Sr_2CuO_3, we predict O Frenkel defects with calculated formation energies per defect of 0.4 eV and -0.1 eV. O vacancies in the *a–b* plane are found to be over 1 eV lower in energy than those along the *c* axis, while the favoured interstitial position is along the *b* axis between the two Cu atoms. Reference to figures 2(*c*) and 2(*d*) shows that this is one of the occupied positions of the tetragonal structure, so that O Frenkel defects might be thought of as representing the initial stages of an order–disorder transition from the orthorhombic to the tetragonal phase. Previous

Table 3. Calculated formation energies of electronic defects in La_2CuO_4, Nd_2CuO_4, Ca_2CuO_3 and Sr_2CuO_3.

Defect	Formation energy (eV)			
	La_2CuO_4	Nd_2CuO_4	Ca_2CuO_3	Sr_2CuO_3
$^lh_{Cu}$	1.8	4.6	4.2	3.9
$^sh_{Cu}$	2.0	4.3	4.7	4.1
^lh_O $(a–b)$	3.0	3.1	3.3	2.4
^sh_O $(a–b)$	3.6	4.2	5.1	4.2
^lh_O (c)	3.0	3.6	3.4	2.5
^sh_O (c)	3.8	4.1	5.0	4.2
$^le_{Cu}$	2.5	−0.7	−0.4	−0.3
$^se_{Cu}$	2.4	−0.9	−0.7	−0.8
Band gap	4.2	2.2	2.6	1.6
Hole–lattice energy	1.1–1.7	1.0–1.7	1.2–1.5	1.2–1.8
Electron–lattice energy	1.2	1.2	1.4	1.5

calculations predicted that O vacancies in La_2CuO_4 (Allan and Mackrodt 1988a, b) are also less energetic at equatorial sites, i.e. in the CuO_2 planes, than those at axial sites by about 1 eV, in agreement with experiment (Nguyen *et al* 1981). While O interstitials do not physically disrupt the CuO_2 chains (figure 2), vacancies do and would be expected to have a deleterious effect on conduction in these chains in much the same way they do in the CuO_2 planes of La_2CuO_4 (Shafer *et al* 1987, Tarascon *et al* 1987, Johnston *et al* 1987).

Lattice calculations allow estimates to be made of the energies of valence band holes and defect or conduction band electrons in the large- and small-polaron limits and also the electron–lattice and hole–lattice coupling energies, which can be used to estimate the McMillan coupling parameter λ and from this T_c in the strong- and weak-coupling limits (Allan and Mackrodt 1988b). In addition to the lattice contribution to the formation energies of defect electrons and holes, the atomic ionisation potentials and band contributions to the large-polaron energies are also required. As before (Allan and Mackrodt 1988a, b, c), the free-ion values have been used for Cu and calculated values of −9.2 eV and 0.2 eV, respectively, for the ionisation potentials of lattice O (Mackrodt and Stewart 1979). Previously, the various band contributions to the large-polaron energies were estimated from the recent band-structure calculations of Mattheiss (1987), Bullett and Dawson (1987) and Temmerman *et al* (1987). The comparable calculations are not available for Ca_2CuO_3 and Sr_2CuO_3. Reference to figure 1(b), however, shows that the CuO_2 chain structure in $YBa_2Cu_3O_7$ (shown shaded) is similar to that of Ca_2CuO_3 and Sr_2CuO_3, shown shaded in figure 2(a), so that we have estimated the relevant band terms from the partial densities of states of the chain Cu and O bands of $YBa_2Cu_3O_7$ (Bullett and Dawson 1987, Temmerman *et al* 1987). For the Cu and O valence bands the contribution to the large polaron is estimated to be 2.0 eV and 3.0 eV respectively, compared with values of 1.4 eV and 2.5 eV for the planar bands in La_2CuO_4. As in La_2CuO_4 the contribution for the Cu conduction band is taken to be 1.0 eV (Allan and Mackrodt 1988a, b).

As table 3 shows, we find the large-polaron O 2p band hole, ^lh_O, to be the most stable hole state in both Ca_2CuO_3 and Sr_2CuO_3, as it is in Nd_2CuO_4. We also find the same difference between the energies of ^lh_O and $^lh_{Cu}$, about 1.5 eV. This contrasts with
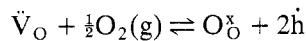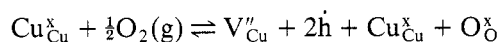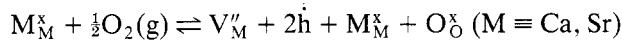
Table 4. Calculated oxidation–reduction defects, energies and p_{O_2} exponents of La_2CuO_4, Nd_2CuO_4, Ca_2CuO_3 and Sr_2CuO_3. $M \equiv La, Cu, Ca, Sr$.

Defect or energy (eV)	La_2CuO_4	Nd_2CuO_4	Ca_2CuO_3	Sr_2CuO_3
E_1	2.2	7.3	2.5	1.6
E_2	4.0	3.9	3.8	2.7
E_3	−1.7	0.1	−0.5	−1.3
Majority defects	$V'''_{La}, \dot{h}$	$V''_{Cu}, \dot{h}$	$O''_i, \dot{h}$	$O''_i, \dot{h}$
$E_f(V_M/O''_i, \dot{h})$	0.6	1.3	0.1	−0.5
p_{O_2}	$\frac{3}{16}$	$\frac{1}{8}$	—	—
$E_f(V''_{Cu})$	2.9	1.3	3.6	3.7
$E_f(V_O^{\cdot\cdot})$	2.8	2.5	0.7	0.3

La_2CuO_4, for which $^1h_{Cu}$ is predicted to be the lowest-energy hole state. However, as emphasised previously (Allan and Mackrodt 1988a, b, c), the differences between the calculated values of ^1h_O and $^1h_{Cu}$ are small in relation to some of the approximations invoked in estimating the formation energy of holes in these materials, so that both types of hole seem likely. Indeed, it has been conjectured (Allan and Mackrodt 1988b, c) that the presence of both types of hole might be a necessary prerequisite for high-T_c behaviour. Defect electrons are predicted to be small polarons in Ca_2CuO_3 and Sr_2CuO_3 and electron–lattice and hole–lattice coupling energies in the range 1.0–1.8 eV. The disproportionation of Cu(II) to Cu(III) and Cu(I) is calculated to require in excess of 3 eV in Ca_2CuO_3 and Sr_2CuO_3, as it is in La_2CuO_4 and Nd_2CuO_4, so that the present calculations suggest that it is unlikely to contribute to electron pairing in these materials.

5. Lattice oxidation

The oxidation state and nature of the associated defects are major factors that control T_c in La_2CuO_4-based superconductors. As before, to assess these, we consider the following reactions:

$$M_M^x + \tfrac{1}{2}O_2(g) \rightleftharpoons V''_M + 2\dot{h} + M_M^x + O_O^x \quad (M \equiv Ca, Sr)$$

$$Cu_{Cu}^x + \tfrac{1}{2}O_2(g) \rightleftharpoons V''_{Cu} + 2\dot{h} + Cu_{Cu}^x + O_O^x$$

$$V_O^{\cdot\cdot} + \tfrac{1}{2}O_2(g) \rightleftharpoons O_O^x + 2\dot{h}$$

with energies E_1, E_2 and E_3, respectively. These are listed in table 4, together with those of La_2CuO_4 and Nd_2CuO_4 for comparison. From this and the calculated O Frenkel energies, we conclude that the majority defects in Ca_2CuO_3 and Sr_2CuO_3 in the presence of oxygen are O interstitials (O''_i) and holes ($\dot{h}$) with effective formation energies of 0.1 eV and −0.5 eV, respectively. In La_2CuO_4, on the contrary, the majority defects are La vacancies V'''_{La} and holes and, in Nd_2CuO_4, Cu vacancies V''_{Cu} and holes. However, an important similarity between Ca_2CuO_3/Sr_2CuO_3 and La_2CuO_4 is that copper vacancies V''_{Cu} are minority defects and O vacancies are predicted to be unstable with respect to the formation of holes, thereby preserving the structure of the conducting CuO_2 planes and chains.

Table 5. Calculated solution energies of Li$_2$O and Na$_2$O in La$_2$CuO$_4$, Ca$_2$CuO$_3$, and Sr$_2$CuO$_3$.

| | Solution energy (eV) | | | | | |
| | La$_2$CuO$_4$ | | Ca$_2$CuO$_3$ | | Sr$_2$CuO$_3$ | |
Impurity	E_{La}	E_{Cu}	E_{Ca}	E_{Cu}	E_{Sr}	E_{Cu}
Li$_2$O	1.5	1.1	0.9	1.7	1.1	1.4
Na$_2$O	−0.1	3.5	−0.1	2.8	−0.5	1.6

6. Cation impurities

Cation impurities are central to the high-T_c behaviour of La$_2$CuO$_4$-based materials. It is now well established that Ca, Sr and Ba substitute in the La sublattice with the formation of holes, which seem to be critical for high-T_c superconductivity. It has been shown previously (Allan and Mackrodt 1988a, b, c) by explicit calculation that it is energetically more favourable for Ca, Sr and Ba to substitute for La with the creation of compensating holes and for Mg to substitute for Cu isovalently, thereby giving an explanation as to why Mg doping does not lead to superconducting materials. It was also predicted (Allan and Mackrodt 1988a, b, c) that Na and K doping would lead to a defect structure comparable with that induced by Ca, Sr and Ba doping and that materials of the type La$_{2-x}$(Na, K)$_x$CuO$_4$ might exhibit superconducting properties. This has now been confirmed experimentally for La$_{2-x}$Na$_x$CuO$_4$, with $x \simeq 0.3$ and $T_c \simeq 30$ K (Subramanian *et al* 1988). Calculations also predicted that Li would substitute for Cu and this too has been confirmed by experiment (Delgado *et al* 1988). Here we have examined the doping of Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$ by Li and Na, for which the relevant reaction is

$$M_M^x + \tfrac{1}{2}X_2O + \tfrac{1}{4}O_2(g) \rightleftharpoons X_M' + \dot{h} + M_M^x + O_O^x$$
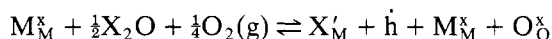
with M ≡ Cu, Ca, Sr and X ≡ Li, Na.

The calculated solution energies E_{Ca}, E_{Sr} and E_{Cu} are given in table 5. Thus we predict that Li will substitute both cation sublattices, albeit unequally, whereas Na will substitute solely for Ca and Sr with the creation of holes and the preservation of the CuO$_2$ chains. Furthermore, in the case of Na, the calculated values of the solution energies suggests solubilities that are comparable with that in La$_2$CuO$_4$ and also with that of Sr in La$_2$CuO$_4$ (Allan and Mackrodt 1988a, b, c).

7. Discussion

The present paper is concerned with the lattice and defect properties of Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$ in relation to their potential high-T_c behaviour. The impetus for it has derived from a fundamental structural issue related to high-T_c behaviour which remains unresolved at present, namely the requisite dimensionality of the superconducting network in ternary and quaternary oxides. La$_2$CuO$_4$-based system contain two-dimensional planes, while those based on YBa$_2$Cu$_3$O$_{6.5+x}$ contain both two-dimensional planes and one-dimensional chains, so that it would clearly be of interest to know whether analogous systems containing only one-dimensional chains could exhibit high-T_c supercon-

ductivity. As before (Allan and Mackrodt 1988a, b, c), our approach is based on a comparison of the relevant lattice and defect properties with those of La_2CuO_4.

The calculated structures of Ca_2CuO_3 and Sr_2CuO_3 are in good agreement with those reported by Teske and Muller-Buschbaum (1969, 1970), with lattice parameters and bond lengths within 2% of the measured values. A higher-energy tetragonal structure has also been calculated for both materials, which, it is suggested might be involved in the defect structures, particularly that of Sr_2CuO_3. Calculations of the thermodynamic stability of the series M_2CuO_3 (M = Mg, Ca, Sr and Ba) find the Ca and Sr compounds more stable with respect to the parent oxides than are the Mg and Ba analogues by approximately 1 eV, in agreement with the known materials. The calculated phonon densities of states show strong peaks at about 15 meV, which, apparently, is characteristic of Cu planar four coordinated by O, for a similar peak is calculated for Nd_2CuO_4 (Allan and Mackrodt 1988c) and found in the experimental spectrum of $YBa_2Cu_3O_7$ (Rhyne *et al* 1987). It has been shown by Weber (1987) that the corresponding peak in La_2CuO_4 at about 10 meV is responsible for electron–phonon coupling and through this to a T_c in the region of 30–40 K, so that Ca_2CuO_3 and Sr_2CuO_3 would appear to have the required dynamical properties for high-T_c behaviour, as suggested previously for Nd_2CuO_4 (Allan and Mackrodt 1988c).

Turning now to the lattice defect structures of Ca_2CuO_3 and Sr_2CuO_3, we find major differences compared with La_2CuO_4 and Nd_2CuO_4 in that O Frenkel defects are predicted, with formation energies that are appreciably lower than those found previously. This suggests a much greater degree of intrinsic disorder in Ca_2CuO_3 and Sr_2CuO_3, which, as discussed later, is also the case in the presence of oxygen. Unlike La_2CuO_4 (Allan and Mackrodt 1988a, b, c), O 2p band holes are calculated to be more stable than Cu 3d band holes, as was found to be the case for Nd_2CuO_4 (Allan and Mackrodt 1988c), although the absolute differences in energy remain small, which suggests the likelihood of both types of hole. It is important to emphasise that the formation energy of large-polaron holes (and electrons) involves band contributions, strictly half the rigid band width for a symmetric band (Catlow *et al* 1977), which we have estimated from the calculated partial densities of states of $YBa_2Cu_3O_7$ (Bullett and Dawson 1987, Temmerman *et al* 1987) in the absence of information on Ca_2CuO_3 and Sr_2CuO_3. This is clearly an approximation which counsels caution in the interpretation of the calculated energies. Thus the *relative* stability of ^1h_O and $^1h_{Cu}$ is unlikely to be affected by more accurate estimates of the band contributions, whereas the *individual* formation energies might be and, through these, the oxidation–reduction and impurity solution energies. However, accepting the present estimates of the various contributions to the defect electron and hole formation energies, our principal findings for Ca_2CuO_3 and Sr_2CuO_3 as far as electronic defects are concerned are that the majority holes are ^1h_O, that defect electrons are small polarons, $^se_{Cu}$, and that electron–lattice and hole–lattice coupling energies are in the range 1.2–1.8 eV. If, therefore, high-T_c behaviour requires Cu 3d band holes with $[^1h_{Cu}] > [^1h_O]$, as in La_2CuO_4, the present calculations suggest that Ca_2CuO_3 and Sr_2CuO_3 are not candidate oxides; on the contrary, if $[^1h_O] \geqslant [^1h_{Cu}]$, as predicted previously for Nd_2CuO_4, is acceptable, then Ca_2CuO_3 and Sr_2CuO_3 might exhibit high-T_c superconductivity under suitable conditions.

The oxidation–reduction characteristics of Ca_2CuO_3 and Sr_2CuO_3 are found to be similar to those of La_2CuO_4, even though the majority defects in the presence of oxygen are different and the degree of disorder greater, with effective formation energies of 0.1 eV and −0.5 eV, respectively. The calculated values of E_1, E_2 and E_3 are close to those of La_2CuO_4, the most significant being that of E_3, from which we predict that O

vacancies are unstable with respect to the formation of hole in the three materials, unlike Nd$_2$CuO$_4$. Since a low O vacancy concentration, which preserves the integrity of the conducting CuO$_2$ planes, has been shown experimentally to be essential for high-T_c behaviour (Shafer *et al* 1987, Tarascon *et al* 1987, Johnston *et al* 1987), this is clearly an important factor in favour of Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$ as potential high-T_c oxides.

The calculated mode of solution predicts that Na will substitute for Ca and Sr with the creation of holes. Furthermore, the magnitude of the solution energies, -0.1 eV and -0.5 eV, respectively, when compared with the effective formation energies of O interstitials and holes in the undoped materials, 0.1 eV in Ca$_2$CuO$_3$ and -0.5 eV in Sr$_2$CuO$_3$, suggests that Na$'_{Ca}$ and $\dot{h}$ will be the majority defects in Na-doped Ca$_2$CuO$_3$, with O$''_i$ as the minority defects, and that Na-doped Sr$_2$CuO$_3$ will contain Na$'_{Sr}$, $\dot{h}$ and O$''_i$ as the principal defects. Since [$\dot{h}$] is controlled by the impurity concentration in both cases through the electro-neutrality equations

$$[\dot{h}] \simeq [\text{Na}'_{Ca}] \qquad (\text{Ca}_2\text{CuO}_3)$$

and

$$[\dot{h}] \simeq [\text{Na}'_{Sr}] + \tfrac{1}{2}[\text{O}''_i] \qquad (\text{Sr}_2\text{CuO}_3)$$

while O interstitials do not disrupt the CuO$_2$ chains, the present calculations suggest that both Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$ will possess impurity defect structures related to high-T_c behaviour that are similar to that of La$_2$CuO$_4$. In summary, then, the calculations reported here indicate that Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$ are similar to La$_2$CuO$_4$ in many important respects, notably the low-energy phonon density of states, non-defective CuO$_2$ planes and chains, unstable O vacancies with respect to the formation of holes and similar aliovalent impurity defect structures. The principal differences is the valence band hole structure, for which the necessary conditions for high-T_c behaviour remain in dispute, with evidence for both Cu 3d band holes (Cu^{3+}) (Alp *et al* 1987) and O 2p band holes (O$^-$) (Tranquada *et al* 1987). Finally, we note that no reference has been made to the necessary electronic structural conditions for high-T_c behaviour in Ca$_2$CuO$_3$ and Sr$_2$CuO$_3$, an investigation into which might be stimulated by the present results.

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