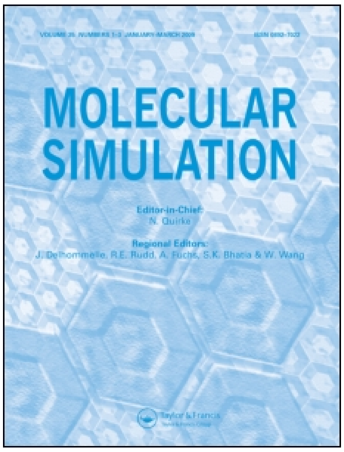

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W. C. Mackrodt[a]
[a] ICI Chemicals & Polymers Ltd, Cheshire, UK

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THE COMPUTER SIMULATION OF SUPERCONDUCTING CERAMIC OXIDES[†]

W.C. MACKRODT

ICI Chemicals & Polymers Ltd, PO Box 8, The Heath, Runcorn,
Cheshire, WA7 4QD, UK.

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This paper is concerned with the application of static and dynamic lattice simulation methods to the new superconducting ceramic materials. An outline is given of the principal lattice features that characterise high T_c oxides, followed by a review of the theoretical and computation methods that have been used previously for treating more traditional ceramic systems. Finally, a summary is given of recent results for La_2CuO_4, compared with the available experimental information.

KEY WORDS: Superconducting materials, ceramics, lattice simulation.

1. INTRODUCTION

For the past decade or so, atomistic lattice simulations, both static and dynamic, have contributed much to understanding the fundamental properties of ceramic oxides [see, for example, articles contained in references 1–5]. The principle reason for this is that with the development of realistic interatomic potentials for a wide variety of materials, it has been possible to calculate directly solid-state properties, many of which are either inaccessible to experiment or obtainable only with extreme difficulty. Thus, computer simulation has been closely associated with, and often an integral part of, the interpretation of convoluted, sometimes incomplete, experimental data. The recent discovery and development of high temperature superconducting oxides have presented a unique opportunity to extend the range of application of these techniques still further, at a time when there is almost unprecidented technological and industrial interest. Accordingly, this paper attempts to identify the features of high T_c materials that are both essential for understanding and amenable to calculation, reviews the theoretical methods used in the appropriate simulations and summarises recent results that have been obtained for La_2CuO_4-based materials.

2. LATTICE FEATURES OF HIGH T_c OXIDES

The simulation techniques used and described in this paper were developed for insulators and semiconductors such as NaCl, CaF_2, MgO and NiO, and not for materials with metallic (or superconducting) properties. It is imperative, therefore, to

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[†] Invited paper.

clarify the validity of their use in the context of high T_c oxides. The essential point is that La_2CuO_4 and the parent oxides of the so-called 123 compounds such as $YBa_2Cu_3O_{6.5}$, in their stoichiometric forms, are neither metallic nor superconducting: it is only when they are doped, as in the case of La_2CuO_4, or made non-stoichiometric, as with $YBa_2Cu_3O_{6.5+x}$, that they exhibit exotic behaviour. Furthermore, there is accumulating evidence that in many of their properites high T_c oxides undergo a continuous change from the semiconducting to the superconducting phase. For example, in $La_{2-x}Sr_xCuO_4$, T_c starts to increase from O K at x ~0.05, reaches a maximum at x ~0.15 and then falls as the concentration of oxygen vacancies increases [6]: there is neither a sharp on-set of T_c(max) at a given value of x nor a sudden fall at some larger value. Similarly, the partial thermodynamic quantities associated with oxidation and reduction vary continuously with x in $YBa_2Cu_3O_{6.5+x}$ across the transition from semi-conducting to superconducting materials. The approach, then, is to calculate (legitimately) the salient lattice and defect properties of the parent oxides (La_2CuO_4, $YBa_2Cu_3O_{6.5}$ etc.), since in any event they determined the doping and stoichiometric characteristics, and from these to deduce the corresponding properties of the superconducting materials.

Atomistic simulations provide a wide range of information on the static and dynamic properties of materials. The particular features that it is suggested relate most directly to high T_c behaviour are:

(i) the lattice structures of the relevant phases, with particular references to the putative low dimensional (super) conducting planes and chains

(ii) the phonon density of states, including the presence (or absence) of the appropriate modes for electron and/or hole coupling

(iii) the nature, energetics, location and migration of the majority lattice defects, particularly oxygen vacancies

(iv) the nature of the electronic defects, especially valence band holes ie whether they are Cu 3d-band (Cu^{3+}) or O 2p-band (O^-) holes and large or small polarons

(v) the magnitude of the electron/hole-lattice coupling energies for estimating the McMillan coupling parameters, λ, and from this, the phonon contribution to T_c

(vi) the oxidation-reduction characteristics, particularly the stability of oxygen vacancies with respect to the formation of holes by the reaction,

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

(vii) the mode of solution of impurities and the nature of the compensating defects, both of which are central to high T_c behaviour in La_2CuO_4 and other ternary and quaternary oxides

(viii) the structure and properties of surfaces and grain boundaries, with particular reference to weak superconducting links in granular materials

(ix) the nature and structure of defects responsible for flux pinning in irradiated single crystals

The majority of these will be discussed in a later section with references to recent work on La_2CuO_4 [7–9].

3. THEORETICAL ASPECTS

3.1 Interatomic Potentials

Interatomic potentials are central to all simulations. In the case of ceramic oxides, the most widely used form suitable for lattice and defect calculations is [10]

$$V_{ij}(r) = Z_iZ_j/r + U_{ij}(r) + P_{ij}(r; F_i, F_j) \tag{1}$$

in which Z_i and Z_j are the ionic charges and U_{ij} and P_{ij} the non-polarised and polarised contributions respectively to the total non-coulombic potential: r is the internuclear separation and F_i and F_j the electric field strengths at the respective ions. A number of simple models have been proposed for calculating P_{ij}, the most convenient being the shell model, which was introduced some time ago by Dick and Overhauser [11] to account for the dielectric properties of the alkali halides. The application of this model in simulation studies has been described in full previously [10, 12].

Two separate approaches have been developed for calculating U_{ij} [10, 12]. The first assumes a specific functional form, which is usually taken as,

$$U_{ij}(r) = A_{ij} . \exp(-B_{ij}/r) + C_{ij}/r^6 \tag{2}$$

and the constants A_{ij}, B_{ij}, C_{ij} found by fitting to experimental data such as the lattice structure, the elastic and dielectric constants and the zone-centre phonon frequencies. For more covalent materials such as SiO_2, bond-bending terms of the form,

$$U_{ijk}(\theta) = D_{ijk}(\theta - \theta_{ijk})^2 \tag{3}$$

have been used [13], in which D_{ijk} is an empirical constant and θ_{ijk}, the equilibrium value of the ijk bond angle. Empirical potentials of this type for La_2O_3, CuO, SrO and BaO have been used by Islam *et al.* [8] in a recent study of the lattice and defect properties of La_2CuO_4.

While empirical potentials of the type referred to above have often proved to be of great value in simulation studies [12], their use can be limited first, by a lack of reliable experimental data, and second, by the inherent inability to treat changes in valence state and interactions involving impurities, for example, in a consistent way. An alternative approach is to calculate U_{ij} directly and here the density-functional method for the homogeneous electron-gas has been found to be most suitable [14]. The essence of the approach is that the total energy of an atomic or molecular system, E, is a unique functional of the electron density, ϱ, [15]

$$E \equiv E[\varrho] \tag{4}$$

For two atomic (ionic) systems a and b at infinite separation, the total energy, E, is

$$E(\infty) = E_a[\varrho_a] + E_b[\varrho_b] \tag{5}$$

and at some finite separation, R,

$$E(R) = E_{ab}[\varrho_a + \varrho_b] \tag{6}$$

Thus the interaction potential, $V_{ab}(R)$, is given by

$$V_{ab}(R) = E_{ab}[\varrho_a + \varrho_b] - E_a[\varrho_a] - E_b[\varrho_b] \tag{7}$$

which relies on the fact that E is a non-linear function of the density. From a computational point of view, the salient point is that atomic densities only are needed, not the combined value. Furthermore, Gordon and Kim [16] have shown how to manipulate the separate functionals E_{ab}, E_a and E_b to achieve maximum accuracy in calculating V^{ab}. The advantage of this approach, bearing in mind the intended use in lattice simulations, are first, that since only atomic densities are needed these can be calculated quite easily for any element in the periodic table to high accuracy. This means that a wide variety of technologically important materials can be considered. Second, electrostatic crystal effects can be built into the atomic densities, and hence into V^{ab}, at least to first order. Third, impurity-host lattice potentials can be calculated in exactly the same way as those for the host-lattice alone. Finally, ions in different valence states can be dealt with in an entirely consistent way. The principal drawback, however, is the complete neglect of covalency effects in the simplest application of the method since it assumes no distortion of the overlapping electron densities. Electron-gas potentials for La_2CuO_4 [9] and other ternary cuprates of the type, M_2CuO_4 (M = Nd, Pr, Al, Y) [17] and M_2CuO_3(M = Mg, Ca, Sr, Ba) [19], have been derived from those of the binary oxides CuO, La_2O_3, Nd_2O_3 etc. and used in recent calculations of lattice and defect properties related to high T_c superconductivity [7,9,17–19].

3.2 *Static Lattice Simulations*

3.2.1 *Non-defective lattice*

At 0 K the structure of a lattice is determined by the condition that it is in mechanical equilibrium ie,

$$\partial E/\partial X_i = 0 \qquad (8)$$

where E is the internal energy, for all the variables, X_i, that define the structure. $\{X_i\}$ comprises the three lattice vectors, $\{R_i\}$, the relative atomic positions in the unit cell, $\{r_i\}$, and, in the case of the shell model, the shell displacements $\{s_i\}$. The latter represent the electronic polarisation of those atoms/ions that are not at a centre of inversion symmetry in the lattice and for highly polarisable ions such as O^{2-} make an appreciable contribution to the stability of the lattice. For complex crystals it is sometimes convenient to minimise the internal energy initially for a subset of $\{X_i\}$, ie $\partial E/\partial r_i = 0$ for fixed $\{R_i\}$, which are often taken as the experimental lattice vectors; however, it is important to emphasise that at 0 K the zero strain structure is determined by equation (8) for all the variables, X_i.

Empirical potentials that are based on experimental structures either reproduce these exactly or come within a few tenths of a percent: for non-empirical potentials, such as those based on the electron gas approximation, the margins of error are normally within the range 1–3% of the observed structures for a wide range of ceramic oxides [14]. Within the context of superconducting ceramics, the crystal structures of a range of ternary cuprates of the type, M_2CuO_4(M = La, Pr, Nd, Y, Al) [9, 17, 18], and M_2CuO_3(M = Mg, Ca, Sr, Ba) [19] have been obtained to better than 3% of the experimental structures and also those of the K_2NiF_4-structured series Sr_2TiO_4, $Sr_3Ti_2O_7$, $Sr_4Ti_3O_{10}$, $SrTiO_3$ [20, 21]. The latter are the analogues of La_2CuO_4, $La_3Cu_2O_7$, $La_4Cu_3O_{10}$, $LaCuO_3$ the evidence for which in La_2CuO_4 – based materials has been reported by Davies and Tilley [22].

3.2.2 *Defective Lattice*

The most convenient approach to the simulation of defects in ionic lattices is that introduced by Lidiard and Norgett [23] and described in detail by Catlow and Mackrodt [24]. The general formulation is based on the notion that the total energy of a defective system is minimised by a relaxation of the nuclear positions and shell displacements of the ions surrounding the defect. It is reasonable to assume that this relaxation is greatest in the vicinity of the defect and that it falls off fairly rapidly at distances away from the defect. This suggests a (notional) partition of a defective crystal into an inner region immediately surrounding the defect, which is appreciably distorted, and an outer region, which is only slightly perturbed. In the former the nuclear positions and shell displacements are obtained by solving the appropriate elastic equations for the force explicitly, whereas those in the latter are estimated from a suitable approximation, the most useful being that suggested 50 years ago by Mott and Littleton [25]. In practice, the outer region is further partitioned into a (finite) near-outer region, in which the Mott-Littleton approximation is used, and a far-outer region which extends to infinity and is treated as a dielectric continuum. The principal problems with this approach are the arbitrary demarcation of the three regions and the size of the inner, explicitly-relaxed lattice. Thus in the context of the general problem of point defects in solids, the two-region approach falls within the class of embedded-cluster models and attempts have been made to include a quantum mechanical description of the inner region [26], albeit of a very small size.

In principle, the relaxed structure (and energy) of a (partitioned) defective crystal could be obtained by minimising the total energy of the system with respect to the nuclear positions and shell displacements in the inner region, as in the case of the perfect crystal. In paractice, however, this is difficult to implement and Norgett [27] has suggested that an alternative approach, which is more tractable, is to minimise the force acting on each ion in the inner region. Writing the variables in the inner and outer regions collectively as x and y respectively, minimising the total energy with respect to x is given by,

$$\mathrm{dE}/\mathrm{d}x = 0 \tag{9}$$

Whereas minimising the force on each atom individually in the inner region is given by

$$\partial \mathrm{E}/\partial x|_{\mathrm{y=constant}} = 0 \tag{10}$$

Rewriting equation (9) as,

$$\mathrm{dE}/\mathrm{d}x = \partial \mathrm{E}/\partial x|_y + \partial \mathrm{E}/\partial y|_x \cdot \partial y/\partial x \tag{11}$$

this reduces to,

$$\mathrm{dE}/\mathrm{dx} = \partial \mathrm{E}/\partial x|_y \tag{12}$$

provided that the ions in the outer region are at equilibrium, ie

$$\partial \mathrm{E}/\partial y|_x = 0 \tag{13}$$

After some manipulation [24], equation (10), which is known as the "force-balance"equation, can be written explicitly in terms of the interatomic potentials acting in the inner and outer regions and solved numerically for the relaxed nuclear positions and shell displacements, from which the energy of the defect is obtained directly [24, 27].

Defect energies which are calculated in this way are sometimes referred to as "thermal energies," for they correspond to lattices in thermal equilibrium, that is to say defective lattices which have relaxed to equilibrium as a result of the thermal motion of the atoms. A variation of the method outlined above, in which only the shell displacements are considered, with fixed nuclear positions, enables an estimate to be made of the so-called "optical energy," which is a measure solely of the electronic response of the lattice to the presence of defect. This is particularly useful in the context of superconducting ceramics (and conducting ceramics more generally) for it enables a quantitive distinction to be made between descriptions of free carriers, either electrons or holes, in the large and small polaron limits and also quantitive estimates of the electron/hole-lattice coupling energies. The lattice contribution to the large polaron energy comprises solely an (electronic) polarsation term, which is obtained by fixing the nuclear positions and allowing only the shell displacements to equilibrate, whereas the small polaron energy includes both the shell displacement and the nuclear relaxation contributions. While the polaron concept is essentially dynamic in nature, since it involves the coupling of the electron/hole charge to the oscillating electric field of a vibrating polar lattice, the use of static lattice calculations can be justified on the grounds that a static description, which is the zero-frequency limit of the dynamic case, contains the essential physics of the problem [28, 29].

The methods outlined in this section have been used by Islam *et al.* [8] and by Allan and Mackrodt [7, 9, 17–19] to calculate the lattice and electronic disorder, oxidation-reduction characteristics, impurity effects and lattice coupling in La_2CuO_4 [7–9] and other ternary cuprates [17–19] of relevance in the context of high T_c superconductivity.

3.3 Dynamic Lattice Simulations

While coupling mechanisms in high T_c superconductors remain the subject of controversy, there is no evidence that phonon coupling does not contribute in all the known materials and some evidence which suggests that it might be totally responsible in La_2CuO_4 – based systems [30]. In the latter, coupling has been attributed to a strong mode at ~ 10 mev, corresponding to the "in-plane" breathing vibration of the four equatorial oxygen atoms, on the basis of the calculated Eliashberg kernal [30] and the measured neutron scattering spectrum [31]. In any event, the phonon spectrum is a useful "fingerprint" of the known high T_c oxides with features that appear to be characteristic of the perovskite structure [19].

Within the lattice dynamics due originally to Born and von Karman and extended by Cochran [32] to include the shell-model, phonon frequencies are obtained from the eigenvalues of the dynamical matrix, *D*, which, in the usual notation [32], is of the form,

$$D = m^{-1/2}(R - TS^{-1}\tilde{T}^{*})m^{-1/2} \tag{14}$$

The vector *m* contains the atomic masses and the matrices *R*, *T* and *S*, the second derivatives of the interactomic potential. *R* contains the core–core interactions, *T*, the core–shell interactions and S, the shell–shell interactions. Thus the second term, $TS^{-1}\tilde{T}^{*}$, is the shell-model contribution to the dynamical matrix and derives from the adiabatic approximation, wherein the electron (shell) distribution follows instantaneously the nuclear positions. Since *D* contains both coulombic and non-coulombic contributions (outlined in section 3.1), the calculation of phonon frequencies, and from these the dispersion relations and density of states (spectrum), is a sensitive test of the interatomic potentials, including the shell parameters. Phonon frequencies are also sensitive to the stability of the lattice and frequently when this is not at equilibrium, ie not at zero strain, imaginary phonon frequencies are obtained. To calculate the electron-phonon interaction, the dynamical matrix, D, is extended to contain a renormalisation contribution, but calculations of this sort are not considered in the present paper. Instead, an alternative approach based on the static coupling energy is used to estimate the McMillan coupling parameter, λ, and from this T_c in the weak coupling limit.

4 RESULTS FOR La_2CuO_4

The calculated lattice parameters of the orthorhombic and tetragonal phases of La_2CuO_4 corresponding to zero bulk and internal strain are given in Table 1 and the basic K_2NiF_4 structure shown in Figure 1. The orthorhombic lattice constants differ

Table 1 Calculated lettice parameters and lattice energies of La_2CuO_4

Parameter/ Energy	*Orthorhombic*	*Tetragonal*
a(A)	5.427(5.406)*	3.783(3.778)
b	5.352(5.370)	–
c	12.994(13.150)	13.050(13.093)
W_L(ev)	−172.71	−172.69

*Values in brackets are the experimental constants reported by Grande *et al.* [47] for the orthorhombic structure and those deduced for the tetragonal structure from the high temperature (420C) constants reported by Longo and Raccah [46]

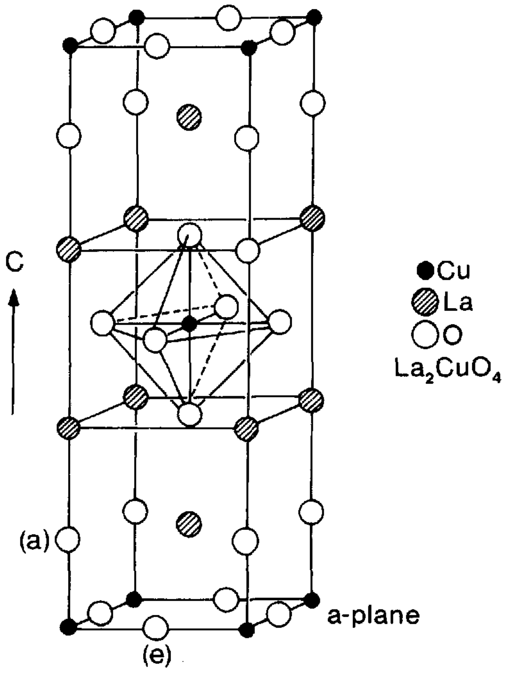

Figure 1 The K_2NiF_4 structure of La_2CuO_4

from the measured values by 1%, or less, and the tetragonal constants by 0.3% or less. Also given in Table 1 are the calculated lattice energies at 0 k. Thus the orthorhombic structure is calculated to be ~2 kJ/mole more stable than the tetragonal simply from the pair-wise interaction and electronic polarisation of the ions, in contrast to, but not in conflict with, the Fermi-surface instability and associated Peierls distortion reported previously [33–35]. Using a classical expression for the Helmholtz free energy, corrected by the zero-point vibration, and the experimental thermal expansion coefficients for the tetragonal phase of $\alpha_a = 12 \times 10^{-6}(C)^{-1}$ and $\alpha_c = 16 \times 10^{-6}(C)^{-1}$, the predicted phase transition temperature is ~250 K, compared with the experimental range ~400 – 500 K, depending on the conditions. At 250 K the enthalpy difference is estimated to be ~1.7 kJ/mole and the (vibrational) entropy difference ~ -0.8 k_B[9], thereby predicting that the phase transition is entropically driven. A third stable structure for La_2CuO_4 has also been calculated: it is of the Nd_2CuO_4 type, with a lattice energy 83 kJ/mole higher than that of the tetragonal phase [17, 18]. Despite their simplicity, therefore, two-body potentials of the type described earlier correctly predict the low temperature phase of La_2CuO_4 and also give a fair estimate of the transition temperature.

Turning now to the dynamic properties of La_2CuO_4, it has already been noted that electron-phonon coupling has been associated with a strong peak at ~10 mev, corresponding to an "in plane" breathing mode of the four equatorial oxygen ions. Reference to Figure 2 shows that a strong peak at this energy is predicted for both phases, with a slight shift to higher energy for the orthorhombic structure. Furthermore, calculations not reported in detail here [36], show that the 10 mev peak is appreciably renormalised in the doped phase, $La_{1.75}Sr_{0.25}CuO_4$, in good agreement with the measured density of states of the superconducting material, $La_{1.85}Sr_{0.15}CuO_4$, [31].

Vacancies are calculated to predominate the lattice disorder, with effective formation energies of 2.2 ev and 1.9 ev per Schottky defect for the orthorhombic and tetragonal phases respectively. However, as shown later, the defect structure is

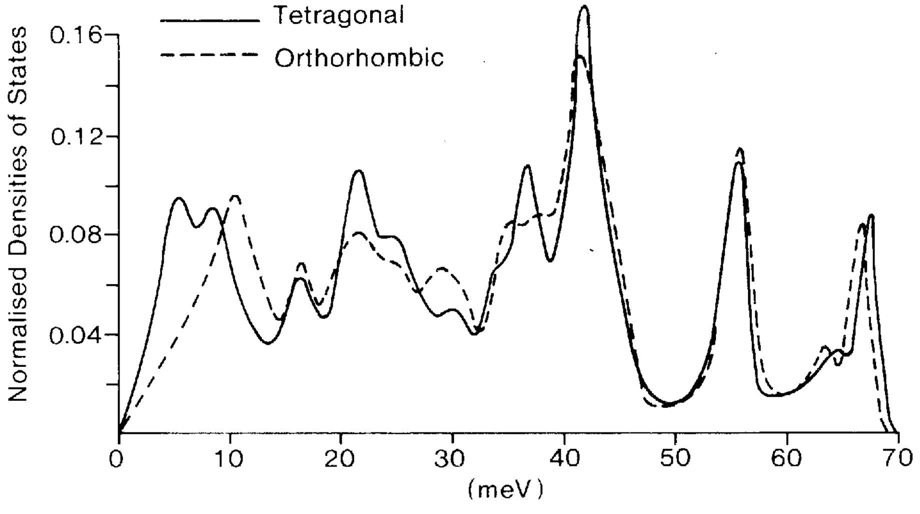

Figure 2 The calculated phonon densities of states of the orthorhombic and tetragonal phases of La_2CuO_4

Table 2 Contributions to the valence band hole energies in La_2CuO_4

Lattice Energies (ev)		
Hole	*Orthorhombic*	*Tetragonal*
${}^{l}h_{Cu}$	−33.7	−34.0
${}^{s}h_{Cu}$	−34.8	−35.1
${}^{l}h_0(e)$	13.9	14.2
${}^{s}h_0(e)$	12.8	13.1
${}^{l}h_0(a)$	14.7	14.7
${}^{s}h_0(a)$	13.0	13.0

Valence band contributions to large polaron hole energies estimated from Mattheiss [33]:

Cu 3d-band 1.4 ev
O 2p-band (e) 1.7 ev
O 2p-band (a) 2.5 ev

Cation ionisation potentials from Weast [47]:

Cu(III) 36.8 ev

Oxygen ionisation potential from Mackrodt and Stewart [14]:

$O^{2-}(I)$ − 9.2 ev

sensitive to the presence of oxygen, the associated defects of which have been found experimentally to be extremely important in controlling T_c in both La_2CuO_4-based superconductors and those related to $YBa_2Cu_3O_{6.5+x}$. An interesting feature to emerge from these calculations and also those reported by Islam *et al.* [8], is that oxygen vacancies at the equatorial sites are predicted to be less energetic than those at the axial sites [7–9]. This is due entirely to differences in the relaxation energy at the two sites. The difference in energy, ~ 1 ev, suggests that at low temperature oxygen vacancies will be more or less confined to equatorial sites, which agrees completely with the experimental data reported by Nguyen *et al.* [37]. Similiar behaviour has been noted in $La_{2-x}(Ca, Sr, Ba)_xCuO_4$ materials [38], and this could explain why T_c is so sensitive to the presence of oxygen vacancies [6, 38], for equatorial vacancies disrupt the putative superconducting "CuO_2" planes, whereas axial vacancies do not.

Electronic defects, particulary valence band holes, have been shown to be closely related to high T_c superconductivity in ceramic oxides and form the basis of proposed alternative mechanisms to phonon-coupling [39–41]. Within the atomistic lattice approach to electronic defects, there are three contributions to the hole energy; a lattice contribution associated with the charged state, ie Cu^{3+} and O^-, which is calculated by the methods described in section 3.2.2, an "effective" ionisation potential of the appropriate lattice ion, which for cations is usually taken to be the free ion value but for oxygen needs to be calculated specifically for the lattice in question [14], and, in the case of large polaron carriers, a band contribution, which represents the kinetic energy of the delocalised hole [9]. Table 2 contains the various contributions to the valence band hole energies in La_2CuO_4 and Table 3 the calculated formation energies. As mentioned previously, the lattice contribution to the large polaron holes, ${}^{l}h_{Cu}$ and ${}^{l}h_0$ (see Footnote), consists solely of the shell displacements (electronic polarisation) with fixed nuclear positions, whereas that to the small polaron description, ${}^{s}h_{Cu}$ and ${}^{s}h_0$, involves both nuclear and shell relaxations. The differences between

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When it is necessary to specify valence band holes in detail, eg *l*arge polaron *C*u 3d-band *h*ole, the notation ${}^{l}h_{Cu}$, ${}^{s}h_O$ etc. will be used: when holes are unspecified, the Kroger-Vink notation, eg h• will be used.

these two lattice contributions correspond to the hole-lattice coupling energies, which are later related to the McMillan parameter and through this to T_c. As shown in Table 3, the energy of the large polaron Cu 3d-band hole, $^{l}h_{Cu}$, is estimated to be ~0.2 ev lower than that of the small polaron and ~1.2 ev lower than that of $^{l}h_0$. Unlike the oxygen vacancy energy, which is predicted to be lower at equatorial sites, the large polaron hole energy is calculated to be identical at the two oxygen sites. It is important to emphasise, however, that while these calculations favour $^{l}h_{Cu}$ over $^{l}h_0$, the approximate nature of the estimates of the ionisation potentials and band contributions given in Table 2, when taken with the relatively small difference in energy between $^{l}h_{Cu}$ and $^{l}h_0$, suggests that the latter must be considered a possibility even as a minority defect. Indeed, it has been suggested that the existence of two types of hole may be a characteristic feature of high T_c materials [9, 18].

It is well-known that oxides containing variable-valence cations are subject to changes in stoichiometry, and hence defect structure, as a result of oxidation and reduction. In the case of La_2CuO_4, the relevant oxidation reactions are

$$La^{x}_{La} + 3/4\,O_2(g) \rightleftharpoons V'''_{La} + 3\,h^{\cdot} + La^{x}_{La} + 3/2\,O^{x}_{O}$$

$$Cu^{x}_{Cu} + 1/2\,O_2(g) \rightleftharpoons V''_{Cu} + 2\,h^{\cdot} + Cu^{x}_{Cu} + O^{x}_{O}$$

$$V^{\cdot\cdot}_{O} + 1/2\,O_2(g) \rightleftharpoons O^{x}_{O} + 2\,h^{\cdot}$$

with associated energies E_1, E_2 and E_3, which are listed in Table 4. From this we conclude that lanthanum vacancies, V'''_{La}, and holes, $h^{\cdot}$, are the lowest energy defects in La_2CuO_4 in the presence of oxygen, with effective formation energies of 0.6 ev and 0.4 ev respectively in the orthorhombic and tetragonal phases. These compare with energies of 2.2 ev and 1.9 ev for the Schottky defects. From the mass-action and electroneutrality equations [9], a p_{O_2} power dependence of 3/16 is deduced for $[V'''_{La}]$ and $[h^{\cdot}]$. Copper and oxygen vacanacies are the minority defects with effective formation energies of 2.9 ev and 2.7 ev for V''_{Cu} in the orthorhombic and tetragonal phases and 2.8 ev and 2.5 ev for $V^{\cdot\cdot}_{O}$. The most significant feature of the oxidation characteristics, as far as high T_c behaviour is concerned, is that oxygen vacanacies are unstable with respect to the formation of holes. As shown later, the doping of La_2CuO_4 by Ca, Sr and Ba leads to substitution of the La-sublattice with the creation of holes as the compensating defects. However, as the concentration of the dopant, and consequently that of the compensating holes, increases, the hole formation energy also increases, thereby increasing the value of E_3. At some critical dopant concentration, therefore, which in the case of Sr doping is ~0.2 per La atom, oxygen vacancies become stable with respect to oxidation: they then form the compensating defects for M_{La}(M = Ca, Sr and Ba) and lead to a decrease in T_c and ultimate loss of superconductivity. Thus the correct oxidation-reduction characteristics are crucial to high T_c behaviour.

Table 3 Calculated hole formation energies (ev) in La_2CuO_4

Hole	*Orthorhombic*	*Tetragonal*
$^{l}h_{Cu}$	1.8	1.5
$^{s}h_{Cu}$	2.0	1.7
$^{l}h_0(e)$	3.0	3.3
$^{s}h_0(c)$	3.6	3.9
$^{h}h_0(a)$	3.0	3.0
$^{s}h_0(a)$	3.8	3.8

Table 4 Calculated oxidation energies (ev) in La_2CuO_4

Energy	*Orthorhombic*	*Tetragonal*
E_1	2.2	1.4
E_2	4.0	3.4
E_3	−1.7	−1.8

As noted earlier, cation impurities are central to the high T_c behaviour of La_2CuO_4-based materials. What lattice simulations are able to provide are the mode and energy of substitution and the nature of the compensating defects, which can be compared with such data that exist or used to predict new high T_c systems [7, 9]. Begining with the alkaline-earth oxides, for these are known to lead to superconducting materials, substitution of the Cu-sublattice can be represented by the defect equation,

$$MO + Cu^{x}_{Cu} \rightleftharpoons M^{x}_{Cu} + Cu^{x}_{Cu} + O^{x}_{O}$$

and that of the La-sublattice by,

$$MO + La^{x}_{La} + 1/2\,O_2(g) = M'_{La} + h^{\cdot} + La^{x}_{La} + 3/1\,O^{x}_{O}$$

bearing in mind that holes, rather than oxygen vacancies, are the predicted compensating defects in stoichiometric La_2CuO_4. The calculated energies of solution are listed in Table 5, from which it is seen that Ca, Sr and Ba are predicted to substitute the La-sublattice with the formation of holes, whereas Mg is predicted to substitute the Cu-sublattice isovalently. Thus, if the creation of valence band holes of whatever type are necessary for high T_c behaviour, as seems to be the case [6], simulations show why the doping of La_2CuO_4 by MgO is not an effective dopant. For Ca, SrO and BaO the low values of the solution energy, also reported by Islam *et al.* [7], suggest high solubility in La_2CuO_4 and this is accords with the known phase diagrams. Turning now to the monovalent oxides, the appropriate defect equations are,

$$1/2\,M_2O + Cu^{x}_{Cu} + 1/4\,O_2(g) = M'_{Cu} + h^{\cdot} + Cu^{x}_{Cu} + O^{x}_{O}$$

and

$$1/2\,M_2O + La^{x}_{La} + 1/2\,O_2(g) = M''_{La} + 2\,h^{\cdot} + La^{x}_{La} + 3/2\,O^{x}_{O}$$

As before, holes, rather than oxygen vacancies are the compensating defects. The calculated solution energies are given in Table 5, from which it is seen that Li is predicted to substitute for Cu and Na for La. While holes are predicted to be created in both cases, Cu substitution disrupts the CuO_2 planes and hence would not be

Table 5 Calculated solution energies (ev), E_{Cu} and E_{La}, of impurity oxides in La_2CuO_4

Impurity	*Orthorhombic*		*Tetragonal*	
	E_{Cu}	E_{La}	E_{Cu}	E_{La}
MgO	0.8	2.4	0.9	1.8
CaO	4.0	0.3	4.6	0.1
SrO	7.3	−0.3	8.2	−0.5
BaO	11.0	−0.1	12.5	−0.2
Li_2O	1.1	1.5	0.9	0.9
Na_2O	3.5	−0.1	3.7	−0.7

expected to lead to high T_c behaviour. Na doping, on the otherland, is predicted to lead to a defect structure which is exactly analogous to that resulting from Sr and Ba doping, and hence to similar high T_c properties [7, 9]. This has recently been confirmed experimentally [42] and represents a modest vindication of the use of lattice simulation methods in the study of superconducting ceramics.

One of the principal advantages and achievements of lattice simulations is that it enables detailed and specific predictions of materials properties. In the case of high T_c oxides the most relevant predictions are clearly those concerning T_c itself. Writing the static hole-lattice coupling energy, ΔE, in the form [9],

$$\Delta E = g^2/Mw^2 \tag{15}$$

in which g is the coupling constant, w an (acoustic) vibrational frequency and M the reduced mass, the McMillan coupling parameter, λ, is given by

$$\lambda = N(0)g^2/Mw^2 \tag{16}$$

$$= N(0)\Delta E \tag{17}$$

For values of ΔE in the range 1.0–1.7 ev, obtained from Table 3, and a value of 0.66 states/ev.cell.spin for N(0) from Mattheiss [33], λ is estimated to be approximately 0.7–1.2. Thus for a Debye temperature, θ_D, of ~300 K [45] and a reduced coulomb interaction, μ^*, of 0.1, the BCS transition temperature, T_c, given by

$$T_c = 0.7\theta_D \exp[-(1 + \lambda)/(\lambda - \mu^*)] \tag{18}$$

is predicted to be in the range from ~12 k to ~28 k for *undoped* La_2CuO_4, in good agreement with the range of temperatures over which Grant *et al.* [44] have found trace superconductivity.

5 SUMMARY

Despite the theoretical simplicity of lattice simulations, the results outlined here indicate that a combination of statics and dynamics based on shell-model potentials correctly predict many of the lattice and defect properties of La_2CuO_4 related to high T_c conductivity. They suggest, therefore, that a wider use of these methods might be made to investigate the necessary structural and dynamic conditions for high T_c behaviour in other known systems and to explore for new and improved materials.

References

[1] "Computer Simulation of solids," edited by C.R.A. Catlow and W.C. Mackrodt, Springer-Verlag, Berlin-Heidelberg-New York, 1982.
[2] "Mass Transport in solids," edited by F. Beniere and C.R.A. Catlow, Plenum, New York, 1983.
[3] "Transport in Nonstoichiometric Compounds," edited by G. Petot-Evas, Hj. Matzke and C. Monty, North-Holland, Amsterdam, 1984.
[4] "Structure and properties of MgO and Al_2O_3," edited by W.D. Kingery, Advances in Ceramics, Volume 10, The American Ceramic Society, Columbus, 1984.
[5] "Nonstoichiometric Compounds," edited by C.R.A. Catlow and W.C. Mackrodt, Advances in Ceramics, Volume 23, The American Ceramic Society, Westerville, 1988.
[6] M.W. Shafter, T. Penney and B.L. Olson, "Correlation of T_c with hole concentration in $La_{2-x}S$-r_xCuO_4 superconductors," *Phys. Rev.*, **B36**,4047 (1987).
[7] N.L. Allan and W.C. Mackrodt "Atomistic lattice calculations of the defect properties of La_2CuO_4

related to high T_c zuperconductivity," *Proc. Mat. Res. Soc. Symp.* **99,** 797 (1988).

[8] M.S. Islam, M. Leslie, S.M. Tomlinson and C.R.A. Catlow, "Computer modelling studies of defects and valence states in La_2CuO_4," *J. Phys.* **C21,** L109 (1988).

[9] N.L. Allan and W.C. Mackrodt, "The calculated defect properties of La_2CuO_4 related to high T_c superconductivity," *Phil. Mag.* (1988) - To be published.

[10] W.C. Mackrodt, "Theory of defect calculations for ionic and semi-ionic materials" in "Mass Transport in Solids," edited by F. Beniere and C.R.A. Catlow, Plenum, New York, 1983.

[11] B.G. Dick and A.W. Overhauser, "Theory of Dielectric Constants of Alkali Halide Crystals," *Phys. Rev.*, **112,** 90 (1959).

[12] C.R.A. Catlow, M. Dixon and W.C. Mackrodt, "Interionic potentials in ionic solids," in "Computer Simulation of Solids," edited by C.R.A. Catlow and W.C. Mackrodt, Springer-Verlag, Berlin-Heidelberg - New York, 1982.

[13] C.R.A. Catlow, C.M. Freeman and R.L. Royle, "Recent studies using static simulation techniques," *Physica.* **131B,** 1 (1985).

[14] W.C. Mackrodt and R.F. Stewart, "Defect properties of ionic solids: II Point defect energies based on modified electron-gas potentials," *J. Phys.*, **C12,** 431 (1979).

[15] P. Hohenberg and W. Kohn, *Phys. Rev.* **136,** B864 (1964).

[16] R.G. Gordon and Y.S. Kim, "Theory of the Forces between Closed-Shell Atoms and Molecules," *J. Chem. Phys.*, **56,** 3122 (1972).

[17] N.L. Allan and W.C. Mackrodt, "Lattice and defect properties of La_2CuO_4, Pr_2CuO_4, Nd_2CuO_4 and Al_2CuO_4 related to high T_c superconductivity," *Proc. Am. Ceram. Soc. Symp.* (1988) - To be published.

[18] 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: relationship to high T^c superconductivity," *Phil. Mag.* (1988) - to be published.

[19] N.L. Allan, J.M. Lawton and W.C. Mackrodt, "Calculated lattice and defect properties of the ternary cuprates, M_2CuO_3(M = Ca, Sr): relationship to La_2CuO_4 and hight T_c superconductivity," submitted to *J. Phys. C.*

[20] G. Burns, F.H. Dacol and M.W. Shafter, 'Raman measurement of materials with the K_2NiF_4 structure," *Solid State Comm.*, **62,** 687 (1987).

[21] N.L. Allan and W.C. Mackrodt - unpublished results

[22] A.H. Davies and R.J.D. Tilley, "New layer structures in the La-Cu-O system," *Nature* **326,** 859 (1987).

[23] A.B. Lidiard and M.J. Norgett, "Point defects in Ionic Crystals," in "Computational Solid State Physics," edited by F.H. Herman, N.W. Dalton and T.R. Koehler, Plenum, New York, 1972.

[24] 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, Sprinter-Verlag, Berlin-Heidelberg - New York, 1982.

[25] N.F. Mott and M.J. Littleton, "Conduction in Polar Crystals I. Electrolytic conduction in solid salts," *Trans. Faraday Soc.*, **34,** 485 (1938).

[26] J.H. Harding, A.H. Harker, P.B. Keegstra, R. Pandey, J.M. Vail and C. Woodward, "Hartree-Fock cluster computations of defect and perfect ionic crystal properties," *Physica.*, **131B,** 151 (1985).

[27] M.J. Norgett, "A general formulation of the problem of calculating the energies of lattice defects in ionic crystals," Report No. *R7650, A.E.R.E.*, 1979.

[28] P.W. Anderson, "Model for the electronic structure of amorphous semiconductors," *Phys. Rev. Lett.*, **34,** 953 (1975).

[29] B.K. Chakraverty, "Bipolarons and superconductivity," *J. Physique.*, **42,** 1351 (1981).

[30] W. Weber, "Electron-Phonon interaction in the new superconductor $La_{s-x}(Ba, Sr)_xCuO_4$," *Phys. Rev. Lett.*, **58,** 1371 (1987).

[31] A.P. Ramirez, B. Batlogg, G. Aeppli, R.J. Cava, E. Reitman, A. Goldman and G. Shirane, "Phonon density of states in $La_{1.85}Sr_{0.15}CuO_4$," *Phys. Rev.*, **B35,** 8833 (1987).

[32] W. Cochran, "Lattice dynamics of ionic and covalent crystals," *Crit. Rev. Sol. St. Sci.*, **2** ,1 (1977).

[33] J. Yu, A.J. Freeman and J.-H. Xu, "Electronically Driven Instabilities and Superconductivity in the layered $La_{s-x}Ba_xCuO_4$ Perovskites," *Phys. Rev. Lett.*, **58,** 1035 (1987).

[34] L.F. Mattheiss, "Electronic Band Properties and Superconductivity in $La_{2-y}X_yCuO_4$," *Phys. Rev. Lett.*, **58,** 1028 (1987).

[35] J.D. Jorgensen, H.-B. Schuttler, D.G. Hinks, D.W. Capone II, K. Zhang, M.B. Brodsky and D.J. Scalapino, "Lattice Instability and High-T_c Superconductivity in $La_{s-x}Ba_xCuO_4$," *Phys. Rev. Lett.*, **58,** 1024 (1987).

[36] N.L. Allan and W.C. Mackrodt - unpublished results (1988).

[37] N. Nguyen, J. Choisnet, M. Hervieu and B. Raveau, "Oxygen Defect K_2NiF_4-Type Oxides: The Compounds $La_{2-x}Sr_xCuO_{4-x/2-}$," *J. Solid State. Chem.*, **39,** 120 (1981).

[38] J.M. Tarascon, L.H. Greene, W.R. McKinnon, G.W. Hull and T.H. Geballe, "Superconductivity at 40 K in the oxygen-deficient perovskites $La_{2-x}Sr_xCuO_{4-y}$," *Science*, **235,** 1373 (1987).

[39] C.M. Varma, S. Schmitt-Rink and E. Abrahams, "Charge transfer excitations and superconductivity in 'ionic' metals," *Solid State Comm.*, **62,** 681 (1987).

[40] V.J. Emery, "Theory of high-T_c Superconductivity in Oxides," *Phys. Rev. Lett.*, **58,** 2794 (1987).

[41] P.W. Anderson, "The Resonating Valence Bond State in La_2CuO_4 and Superconductivity," *Science*, **235,** 1196 (1987).

[42] M.A. Subramanian, J. Gopalkrishnan, C.C. Torardi, T.R. Askew, R.B. Flippen, A.W. Sleight, J.J. Lin and S.J. Poon, *Science*, **240,** 495 (1988).

[43] J. Ruvalds, "Are plasmons and key to superconducting oxides ," *Nature*, **328,** 299 (1987).

[44] P.M. Grant, S.S.P. Parkin, V.Y. Lee, E.M. Engler, M.L. Ramirez, J.E. Vazquez, G. Lim, R.D. Jacowitz and R.L. Greene, "Evidence for Superconducitivity in La_2CuO_4," *Phys. Rev. Lett.*, **58,** 2482 (1987).

[45] B. Grande, Hk. Muller-Buschbaum un M. Schweizer "Zur Kristallstructur von Seltenerdmetalloxocupraten: La_2CuO_4, Gd_2CuO_4," *Z. Anorg. Allg. Chem.*, **428,** 120 (1977).

[46] J.M. Longo and P.M. Raccah, "The Structure of La_2CuO_4 and $LaSrVO_4$," *J. Solid State Chem.*, **6,** 526 (1973).

[47] R.C. Weast (editor), "Handbook of Chemistry and Physics," C.R.C. Press (1979).