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LETTER TO THE EDITOR

Computer modelling studies of defects and valence states in La_2CuO_4

M S Islam†, M Leslie‡, S M Tomlinson§ and C R A Catlow§

† Department of Chemistry, University College London, Gower Street, London WC1E 6BT, UK
‡ SERC Daresbury Laboratory, Warrington, WA4 4AD, UK
§ Department of Chemistry, University of Keele, Keele, Staffs ST5 5BG, UK

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Abstract. Inter-atomic potential models have been derived for La_2CuO_4. The models correctly reproduce the structure of the orthorhombic phase, and yield calculated phonon dispersion curves showing a soft mode. Defect simulations show a large energy barrier to the Cu^{2+} disproportionation reaction, but find that doping of the material and oxidation of the doped material are energetically favoured. The calculations show that the latter takes place with formation of Cu^{3+} ions. Bipolaron formation is also investigated.

The recently discovered high-temperature superconducting oxide materials $La_{2-x}Ba_xCuO_{4-y}$ (Bednorz and Müller 1986) and $YBa_2Cu_3O_{7-x}$ (Wu *et al* 1987) pose important questions concerning the cation valence states, the defect structure and redox processes, and the nature of the electron–lattice interactions and of electron–electron coupling mechanisms. In this Letter we report the results of simulation studies of the pure and doped La_2CuO_4 material, which give insight into all these problems. Simulation methods by their nature cannot yield details of electronic structure, where band theory is the more appropriate technique. They are, however, well suited to probing defect structures and to calculating polarisation energies in polar compounds. The latter, we believe, could play a major role in determining the behaviour of the superconducting oxides. Indeed our calculations show that the polarisation energies associated with the oxidation of Cu^{2+} to Cu^{3+} are large, and we suggest that the interaction between the polarisation fields could provide a coupling mechanism. Our survey of defect energies finds that doping of La_2CuO_4 with divalent cations will lead to oxygen vacancy compensation, but that oxidation of the resulting compounds is exothermic with the creation of Cu^{3+} ions—a result which accords with experiment.

Two types of simulation method are used (see, for example, Catlow 1986). First, energy minimisation studies of the perfect lattice are performed, using standard minimisation procedures to generate an equilibrium structure. The elastic, dielectric and lattice dynamical properties may then be calculated. The present work used the THBREL code (Leslie 1988) for these simulations. Secondly, we performed Mott–Littleton calculations employing the CASCADE code (Leslie 1982) of the formation energies of lattice defects. These included Cu^{3+}, Cu^{+}, and O^{-} substitutionals, the energies of which are needed to predict the stable valence state of the superconducting material. We used the structure given by Grande *et al* (1977), who present their results using space group A*bma*. We transformed their coordinates into space group C*mca* to obtain the *C*-centred unit cell. This effects a cyclical permutation of the Cartesian axes.

The inter-atomic potentials were taken from the relevant binary oxides, i.e. La_2O_3, BaO, SrO and CuO. For the first three oxides we used the parameters reported by Butler *et al* (1983) and by Lewis and Catlow (1985). It was necessary to derive a potential for CuO. This was achieved by a standard empirical least-squares fitting procedure using structural and dielectric data for CuO (Asbrink and Norrby 1970, Guntherschultze and Keller 1932). We found that a satisfactory model for this material must extend beyond the pair potential approximation. We used the bond-bending formalism applied successfully to α-SiO_2 (Sanders *et al* 1984, Catlow *et al* 1985). This adds a term of the type

$$E = \tfrac{1}{2}k_B(\theta - \theta_0)^2$$

to specified bond angles of equilibrium values θ_0. In the present case bond-bending terms were used for O(1)–Cu–O(1) ($\theta_0 = 90°$) and Cu–O(2)–O(1) ($\theta_0 = 38°$), where O(1) and O(2) represent equatorial and axial oxygen atoms, as shown in figure 1. We note that ion polarisation is modelled using the shell model of Dick and Overhauser (1958). The potential parameters for the interactions involving Cu^+, Cu^{3+} and O^- were obtained semi-empirically by the 'shifted electron-gas' method (Murray 1985).

All potential parameters used in the study are reported in table 1.

The potential model yields an equilibrium structure for La_2CuO_4 (see figure 2) which is close to that observed experimentally. Table 2 gives calculated and experimental bond lengths. The deviation is generally small, the largest discrepancy of ~0.1 Å being for the

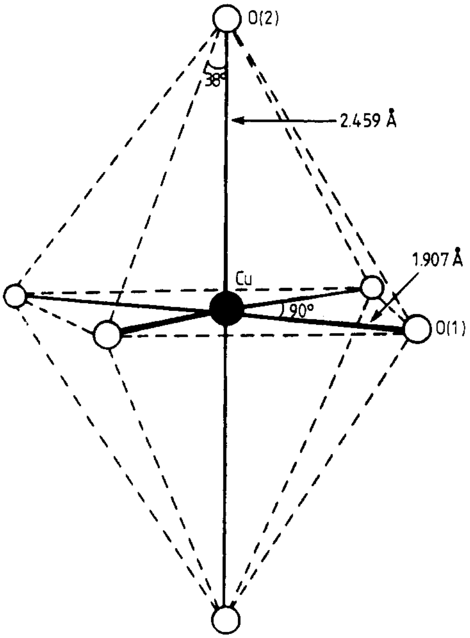

Figure 1. Axially distorted CuO_6 unit in La_2CuO_4. Angles around which bond-bending potentials operate are shown (after Grande *et al* (1977)).

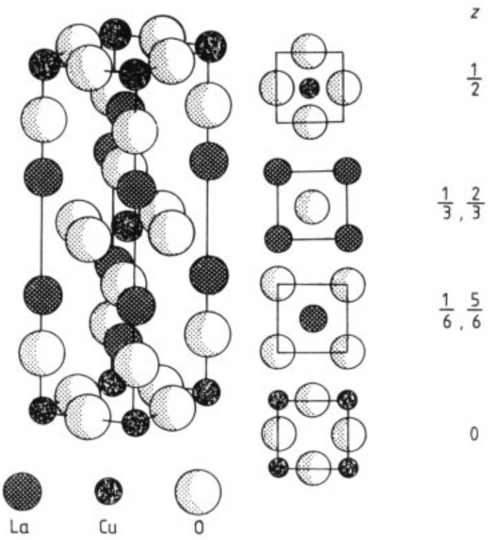

Figure 2. The structure of La_2CuO_4 (after Yu *et al* (1987)).

Table 1. Potential parameters. In (*a*) the potential cutoff = 1.25 lattice units.

(*a*) Short range Interaction	A (eV)	ρ (Å)	C (eV Å^{-6})
$La^{3+} \ldots O^{2-}$	1644.98	0.36196	0.0
$Cu^{+} \ldots O^{2-}$	194.54	0.43188	0.0
$Cu^{2+} \ldots O^{2-}$	294.15	0.40023	0.0
$Cu^{3+} \ldots O^{2-}$	583.93	0.35402	0.0
$Cu^{2+} \ldots O^{-}$	92.81	0.4635	0.0
$Ba^{2+} \ldots O^{2-}$	1214.4	0.3522	8.0
$Sr^{2+} \ldots O^{2-}$	959.1	0.3721	0.0
$O^{2-} \ldots O^{2-}$	22764.3	0.1490	43.0

(*b*) Shell model	Species	Y ($\lvert e \rvert$)	k (eV Å^{-2})
	La^{3+}	−0.25	145.0
	Cu^{2+}	1.0	10^5
	Ba^{2+}	1.848	29.1
	Sr^{2+}	3.251	71.7
	O^{2-}	−2.389	42.0

(*c*) Three-body	Central atom	k_B (eV rad^{-2})	θ_0
	Cu	2.1889	90
	O(2)	3.2813	38

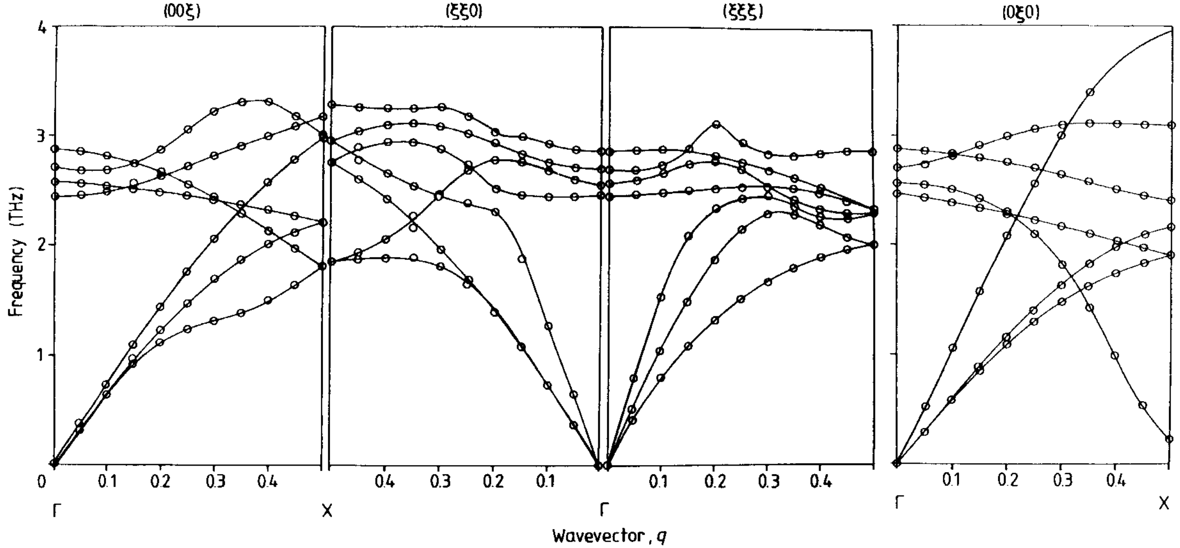

Figure 3. Calculated phonon dispersion curves for La_2CuO_4. The first three panels constitute figure 3(*a*); the right-hand panel is figure 3(*b*).

Table 2. Composition of calculated and observed bond lengths in La_2CuO_4.

Bond	r_{exp} (Å)[a]	r_{calc} (Å)	Difference Δ (Å)
Cu–O(1)	1.907	1.906	0.001
Cu–O(2)	2.459	2.366	0.093
La–O(1)	2.681	2.658	0.023
	2.592	2.599	0.007
La–O(2)	2.304	2.409	0.105
	2.652	2.584	0.068
	2.766	2.743	0.023
	2.900	2.934	0.034

[a] Grande *et al* 1977.

La–O(2) bond; refinement of the La–O potential would very probably remove this small problem.

We also performed calculations of the phonon dispersion curves. The results are presented in figure 3. We note that all branches yield positive frequencies indicating that our potential model is fully stable. However, we find that for phonons along the *b* direction of the unit cell a softening of one of the branches is calculated (see figure 3(*b*)). The direction of the soft phonon mode is along the long O–Cu–O axis. We note that there has been considerable speculation as to phonon mode softening in superconducting oxides. Lattice dynamical calculations (Weber 1987) have suggested softening of one of the acoustic branches. The latter authors also suggest that a relatively small number of phonon modes show strong interaction with the conduction electrons. Furthermore, a recent neutron study of a single crystal of La_2CuO_4 measured a soft optical phonon mode that agrees very closely with our calculated behaviour (Birgeneau *et al* 1987). However, our calculated eigenvectors indicate that the ion displacements associated

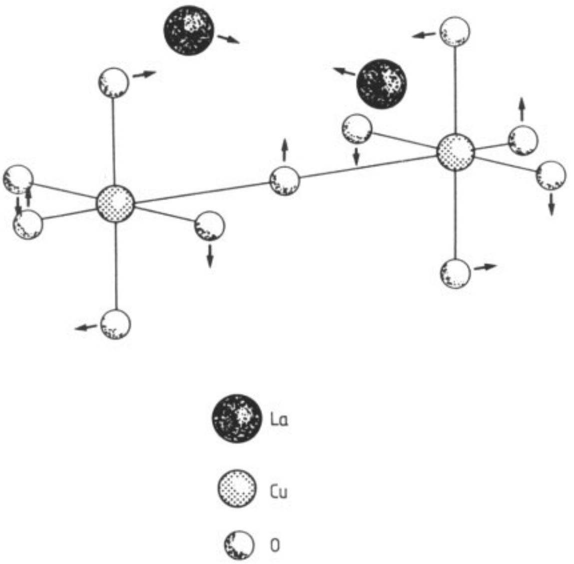

Figure 4. Ion displacements associated with our predicted soft phonon mode.

with the soft mode do not represent a simple rotation of the CuO_6 octahedra, as Birgeneau and co-workers suggest. The direction of the displacements we calculate are shown schematically in figure 4, the copper ion being stationary.

There is little doubt that with an improved range of experimental physical properties it will be possible to refine our potential models. The present results suggest, however, that useful calculations can be performed with currently available models.

Our calculated energies for Cu^{3+}, Cu^{+} and O^{-} substitutionals are reported in table 3 together with results for oxygen vacancies and Ba and Sr dopant ions. For the Cu^{3+}, Cu^{+} and O^{-} substitutional species we give results first for calculations in which a full equilibration of the lattice surrounding the defect species has been performed (referred to as 'thermal' calculations), and secondly for the case where relaxation of just the shells has been performed (referred to as 'optical' calculations). In the latter case we report the magnitude of the polarisation energy which we may equate to the purely *electronic* polarisation surrounding the defect, while the difference between the optical and thermal calculations gives the *displacement* polarisation energy. We note that both electronic and displacement polarisation energies reported in the table are substantial (~3 eV); the magnitudes indicate the strength of electron–lattice interaction in this polar oxide.

From examination of the vacancy energies it is clear that it is energetically more favourable to form oxygen vacancies in equatorial rather than axial positions.

By combining the energies reported in table 3 with appropriate ionisation energies and electron affinities (also reported in the table) it is possible to estimate the energies

Table 3. (*a*) Formation energies of isolated defects and substitutionals. (*b*) Atomic and lattice energies. Key: I_2 and I_3 are the second and third ionisation potentials of copper; E_1 and E_2 are the first and second electron affinities of oxygen; D_e is the dissociation energy of an O_2 molecule.

(*a*) Formation energies

Species	Energy (eV) Thermal	Energy (eV) Optical	Electronic polarisation energy (eV)	Displacement polarisation energy (eV)
Cu^{+}	21.68	24.37	3.38	2.69
Cu^{3+}	−33.92	−31.22	3.07	2.70
$O^{-}(1)$	14.19	17.19	2.03	3.00
$O^{-}(2)$	14.75	18.22	1.82	3.47
$V_O^{\cdot\cdot}(1)$	15.93			
$V_O^{\cdot\cdot}(2)$	17.73			
Ba_{La}'	24.09			
Sr_{La}'	21.38			

(*b*) Atomic and lattice energies

Term	Energy (eV)
I_2	20.39
I_3	36.83
E_1	1.47
E_2	−8.75
D_e	5.16
$E_{Lat}(BaO)$	−31.25
$E_{Lat}(SrO)$	−33.42
$E_{Lat}(La_2O_3)$	−126.12

Table 4. Energies of hole formation, charge transfer, solution and oxidation processes.

Process		Energy (eV)
Total formation energy for Cu^{3+} ion	Thermal	2.91
	Optical	5.61
Total formation energy for O^- ion	Thermal	5.44
	Optical	8.44
$2Cu^{2+} \rightarrow Cu^+ + Cu^{3+}$	Thermal	4.20
	Optical	9.59
$BaO \rightarrow Ba'_{La} + \frac{1}{2}V_O^{\cdot\cdot} + \frac{1}{2}La_2O_3$	Thermal	0.25
$SrO \rightarrow Sr'_{La} + \frac{1}{2}V_O^{\cdot\cdot} + \frac{1}{2}La_2O_3$	Thermal	−0.29
$V_O^{\cdot\cdot} + \frac{1}{2}O_2 \rightarrow O_O^x + 2Cu_{Cu}^{\cdot}$	Thermal	−0.25

of formation of Cu^{3+}, Cu^+ and O^- species (with respect to electrons in the vacuum). The results are given in table 4, again for both thermal and optical processes. Examination of the results show that the formation of Cu^{3+} is energetically preferred to that of O^-. Oxidation of the doped material will therefore lead to the formation of the former species.

It is also possible to combine these calculated values to obtain estimates of the energies of important reactions. The three we consider are listed below.

(i) The charge transfer reaction:

$$2\,Cu^{2+} \rightarrow Cu^+ + Cu^{3+}.$$

(ii) The dopant solution reaction:

$$MO \rightarrow M'_{La} + \frac{1}{2}V_O^{\cdot\cdot} + \frac{1}{2}La_2O_3$$

where M represents either Sr or Ba.

(iii) The oxidation reaction:

$$V_O^{\cdot\cdot} + \frac{1}{2}O_2 \rightarrow O_O^x + 2Cu_{Cu}^{\cdot}$$

where we assume that oxidation takes place by the filling of vacancies created to compensate for the charge of the dopant ions and with creation of Cu^{3+} ions.

In calculating the oxidation energy we have used the value for the small-polaron species in which stabilisation by displacement polarisation is included. If there is greater stability for the large polaron (in which only electronic polarisation is operative, but which is stabilised by roughly half the band width), then our calculated energy of oxidation will be insufficiently negative. We note that the calculated solution and redox energies require the lattice energies of the divalent oxides and the dissociation energy of the O_2 molecule. The values used are given in table 3(*b*).

The resulting calculated energies show first that the copper disproportionation reaction is energetically unfavourable, and indeed the magnitude of the relaxation energy is such that it is unlikely that this charge transfer process is of any significance in this material. The calculated solution energies of SrO and BaO in La_2CuO_4 accord with the observation that divalent oxides dissolve readily in this material. The energy calculated for the oxidation reaction is of particular interest. The negative value, indicating an

Table 5. Energies of bipolaron formation.

Bipolaron configuration	Energy (eV)		Binding energy (eV)	Polarisation energy (eV)	Change in polarisation energy (eV)
A	Thermal	−67.53	0.49	14.57	3.03
	Optical	−61.06	1.25	8.10	1.96
B	Thermal	−67.48	0.33	14.51	2.97
	Optical	−61.07	1.14	8.10	1.96
C	Thermal	−67.63	0.18	13.88	2.34
	Optical	−61.48	0.93	7.73	1.59
D	Thermal	−67.61	0.15	13.67	2.13
	Optical	−61.58	0.82	7.64	1.50

exothermic reaction, clearly accords with experiment as it is known that the doped material readily oxidises with annhilation of vacancies.

It is of interest to investigate the interaction between Cu^{3+} ions and to test whether there is any possibility of coupling between these species to form 'bipolarons'. A number of configurations have been studied for which results are reported in table 5. Model A has two Cu^{3+} ions in the same layer at a distance of about 5.5 Å; model B has the two Cu^{3+} ions along the *c* axis at a distance of 5.5 Å; model C has the two Cu^{3+} ions in adjacent layers but at a separation of 8 Å; model D also has the two Cu^{3+} ions in adjacent layers but now with a larger separation of 8.5 Å. The energies for these pair configurations reported in table 5 refer to both thermal and optical calculations. Binding energies with respect to isolated substitutional Cu^{3+} ions are also presented. The change in polarisation energies, both displacement and electronic, may also be calculated; values are given in table 5. We find that none of the pairs are bound. However, we do find, as expected, that the polarisation energy strongly favours coupling of the pairs, and it may be that screeening effects, which are not adequately included in our treatment, could reduce the Coulomb repulsion energies and result in stable bipolarons.

We have shown that modelling methods provide a useful way of investigating defect energies and valence state stabilities in superconducting oxides. Our work emphasises the important role of polarisation energies in these materials. Further studies will investigate bipolaron formation in greater detail and will extend our work to the $YBa_2Cu_3O_7$ material.

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