Defects and Holes in the Mercury-based Oxide Superconductors: Relevance to High T_c Behaviour

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Calculations on the mercury-based oxide superconductors using computer simulation techniques predict that oxidation to create the holes necessary for superconductivity is highly favourable; our results are relevant to high T_c behaviour and accord well with the available experimental data.

The newly discovered Hg-based oxides with general formula $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ have the highest superconducting transition temperature (T_c) for any known superconductor.[1–4] The three-layer compound, $HgBa_2Ca_2Cu_3O_{8+\delta}$, has set a record T_c of 135 K or up to 160 K under high pressure.[5] As with other cuprate superconductors, their complex structures are based on oxygen-deficient perovskite units comprised of the (super)-conducting CuO_2 planes (Fig. 1).

It is now clear that defect processes play a vital role in determining the properties of the superconducting oxides. For example, the T_c of both $La_2CuO_{4+\delta}$ and $YBa_2Cu_3O_{7-\delta}$ is strongly influenced by the extent of oxygen non-stoichiometry. For the Hg-based oxides, it is believed that excess oxygen atoms (as interstitial defects) are the primary doping mechanism to create the positive 'holes' necessary for superconductivity. Diffraction experiments have already shown that the oxygen interstitials are present at the $[\frac{1}{2}\,\frac{1}{2}\,0]$ site in the centre of the Hg plane.[1,3,6–9] However, some studies have found an additional defect involving partial substitution of Hg by Cu coupled to the presence of oxygen at the $[\frac{1}{2}\,0\,0]$ position between the Hg(Cu) atoms.[6,9] These two types of defect are shown in Fig. 1. Important questions, therefore, remain concerning the precise defect structure and the nature of the redox reaction responsible for the generation of the superconducting holes. In an attempt to gain further insight into these problems we have investigated the Hg-based oxides using computer simulation techniques; these are now well-tested tools for probing solid-state properties at the atomic level and have been successfully applied to other complex oxides[10] and to the study of oxygen interstitials in cuprate superconductors.[11]

Since the simulation techniques have been described comprehensively elsewhere,[12] only a brief overview is given here. The calculations were carried out using energy minimization procedures embodied in the CASCADE code.[13] The interatomic potentials are based on the Born model of the solid, which includes a long-range Coulombic interaction, and a short-range term to model overlap-repulsions and van der Waals forces; the electronic polarisability of the ions is described by the shell model.[12] For the first three members of the homologous series, namely $HgBa_2CuO_{4+\delta}$ (referred to as Hg-1201), $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223), the potential parameters were derived simultaneously by empirical methods which resulted in a common set of interatomic potentials.[14] This approach enables some information concerning the curvature of the energy surface to be included and has the added advantage of improved transferability. It should be stressed, as argued previously,[12] that employing such a model does not necessarily mean that the electron distribution corresponds to a fully ionic system, and that the general validity of the potential model is assessed primarily by its ability to reproduce observed crystal properties. In practice, it is found that models based on formal charges work well even for some semi-covalent compounds such as silicates and zeolites.

The defect energies were simulated using the generalised Mott–Littleton approach in which the ions in an inner region around the defect were relaxed explicitly, and ions further from the defect were treated using a continuum method.[12] Prior to carrying out the defect calculations, energy minimization of the perfect lattice was performed to generate a completely relaxed equilibrium structure. The calculated and experimental lattice parameters are listed in Table 1 which reveals good agreement between simulated and observed structures.

To pinpoint the precise defect position, calculations were first performed on the energies of isolated oxygen interstitials in all three mercury compounds. As well as the O(4) $[\frac{1}{2}\,\frac{1}{2}\,0]$ and O(5) $[\frac{1}{2}\,0\,0]$ sites, we have also considered a position between Cu(1) and Cu(2) as has been noted in some bismuth cuprates. The resulting energies are given in Table 2. In all cases, the lattice

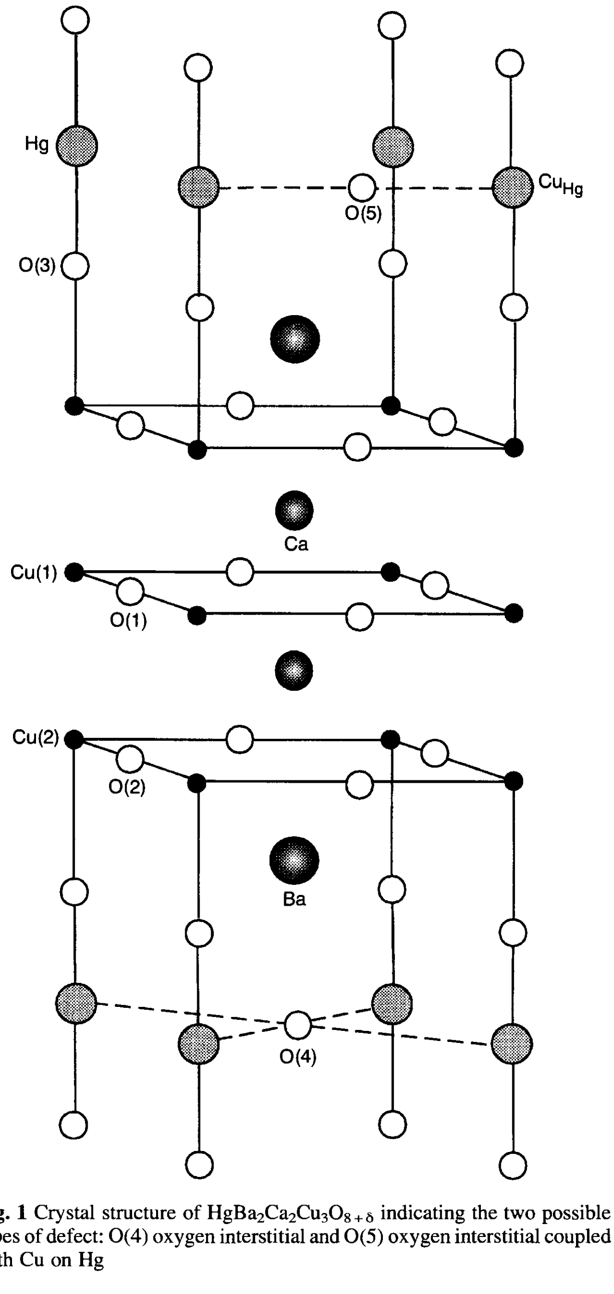

Fig. 1 Crystal structure of $HgBa_2Ca_2Cu_3O_{8+\delta}$ indicating the two possible types of defect: O(4) oxygen interstitial and O(5) oxygen interstitial coupled with Cu on Hg

ions surrounding the defect are allowed to relax in the energy minimization procedure. From examination of the interstitial energies it is clear that it is relatively more favourable to form an isolated oxygen interstitial on the O(4) site located at the centre of the Hg layer, in accord with neutron diffraction studies of Wagner *et al.*[6] and Chmaissem *et al.*[7] It is interesting to note that the difference between O(4) and O(5) energies increases from Hg-1201 to Hg-1223, which is not too surprising in view of the corresponding decrease in the *a*-axis lattice parameters. Our results also suggest that the oxygen interstitial site between the two Cu–O layers is unlikely to be of any significance in these materials.

We then addressed the problem of the anti-site defect involving partial substitution of Cu^{2+} for Hg^{2+} coupled with the presence of oxygen on the O(5) [$\frac{1}{2}$ 0 0] site. Calculations were performed on an 'isolated' Cu_{Hg} substitutional and on a defect complex comprised of two near-neighbour Cu_{Hg} to the O(5) oxygen interstitial (shown in Fig. 1). The results are reported in Table 2 which gives the cluster binding energy with respect to the component defects, where our sign convention is such that a negative value indicates the system is bound. The calculations reveal that the substitution of Hg by Cu is energetically unfavourable as an isolated defect. However, the strong binding energies for the defect cluster suggests that the O(5) interstitial is stabilised by neighbouring Cu_{Hg} substitutionals. Since there is no Coulombic interaction for this isovalent substitution, the coupling is largely due to lattice relaxation and polarization associated with the constituent defects. Recent thermogravimetric analysis (TGA) measurements have found that the occupancy of the O(5) site in Hg-1223 is essentially constant under oxidizing or reducing conditions,[6] and propose that the O(5) oxygen is more strongly bound to the Cu than the oxygen atoms at O(4). Our calculated binding energies are consistent with this observation. In this context, we should note that the magnitude of the isolated Cu_{Hg} substitutional energy (*ca.* 1.4 eV) is comparable to the favourable binding energy of the cluster (−1.2 to −1.5 eV) for all three systems. It is therefore possible that a subtle equilibrium exists between these two configurations which would be sensitive to synthesis conditions; this point is clearly relevant to why this defect is observed in some samples[6,9] but not in others.[7]

As is the case with $YBa_2Cu_3O_{6+\delta}$, the itinerant charge-carriers in the mercury cuprates are believed to be extrinsically generated by incorporation of additional oxygen. In terms of defect chemistry, the oxygen 'excess' is accommodated at interstitial sites with compensation by hole formation. This important oxidation reaction may be formulated as eqn. (1).

$$\tfrac{1}{2}O_{2(g)} + 2Cu_{Cu} \rightleftharpoons O_i'' + 2Cu_{Cu}^{\bullet} \qquad (1)$$

where, in Kroger–Vink notation, O_i'' is a doubly-charged oxygen interstitial and $Cu_{Cu}^{\bullet}$ is a Cu^{3+} hole. Our studies have favoured copper holes over oxygen holes[14] although we acknowledge that the question of whether such species have predominantly Cu(3d) or O(2p) character remains controversial. Nevertheless, our main concern here is to understand how hole species might form; for this task our simulation procedures have proved to be reliable. Ultimately, it will be necessary to employ quantum mechanical methods to examine the stability of electronic states in these materials. The merit of our simulation approach is that it includes detailed estimates of lattice polarization and Coulomb energies which are difficult to make from other sources. The energies of the oxidation reaction (1) were calculated and are reported in Table 3.

Three main points emerge from these results. First, the negative values, indicating highly favourable reactions, clearly accord with observation as it is known that these materials readily oxidize with the uptake of oxygen. Our results therefore confirm that this reaction is responsible for the generation of charge-carriers (holes) necessary for superconductivity in these

Table 1 Calculated and experimental lattice parameters (Å) of the Hg-based superconductors (space group *P*4/*mmm*)

Compound		Calculated[a]	Experimental[b]
$HgBa_2CuO_{4+\delta}$	*a*	3.936	3.875
	c	9.413	9.513
$HgBa_2CaCu_2O_{6+\delta}$	*a*	3.869	3.855
	c	12.659	12.665
$HgBa_2Ca_2Cu_3O_{8+\delta}$	*a*	3.845	3.850
	c	15.885	15.784

[a] δ = 0. [b] Experimental values of δ = 0.06, 0.22 and 0.27 for Hg-1201, Hg-1212 and Hg-1223, respectively (refs. 6,7).

Table 2 Calculated defect energies: Isolated oxygen interstitials

	Energy/eV[a]		
Interstitial site	$HgBa_2CuO_{4+\delta}$	$HgBa_2CaCu_2O_{6+\delta}$	$HgBa_2Ca_2Cu_3O_{8+\delta}$
O(4) [$\frac{1}{2}$ $\frac{1}{2}$ 0]	−18.20	−19.86	−20.98
O(5) [$\frac{1}{2}$ 0 0]	−18.03	−19.29	−20.20
Ca layer [0 0 z]	—	−13.25	−14.09

Isolated substitutional and defect cluster

	Energy/eV		
Defect	$HgBa_2CuO_{4+\delta}$	$HgBa_2CaCu_2O_{6+\delta}$	$HgBa_2Ca_2Cu_3O_{8+\delta}$
Cu_{Hg} substitutional	1.40	1.38	1.37
[$2Cu_{Hg}$ O(5)] cluster[b]	−1.18	−1.19	−1.49

[a] Zero reference at infinity. [b] Negative binding energy (per Cu) indicates system is bound.

Table 3 Energies of the oxidation process to form hole species

	Energy/eV		
Process	$HgBa_2CuO_{4+\delta}$	$HgBa_2CaCu_2O_{6+\delta}$	$HgBa_2Ca_2Cu_3O_{8+\delta}$
$\frac{1}{2}O_{2(g)} + 2Cu_{Cu} \rightarrow O_i'' + 2Cu_{Cu}^{\bullet}$	−1.47	−1.82	−2.25

oxides. Second, the most favourable oxidation energy is found for the highest T_c material, $HgBa_2Ca_2Cu_3O_{8+\delta}$, suggesting a wider range of oxygen excess (δ) in this system, as is the case. Moreover, we find good quantitative agreement with a measured oxidation enthalpy of -136 kJ mol^{-1} (-1.41 eV) for $HgBa_2CuO_{4+\delta}$ derived from recent oxygen annealing experiments;[15] this provides encouraging support for the general validity of our modelling approach.

In summary, we have illustrated that by employing an accurate potential model together with advanced simulation techniques, we can study key properties that are clearly relevant to high T_c behaviour in the Hg-based superconductors. The most important result is the prediction that the oxidation process involving oxygen incorporation is highly favourable, and, indeed, supports models in which this mode of hole creation is the necessary prerequisite for p-type superconductivity in these compounds.

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