LETTER TO THE EDITOR

The structure and energies of peroxy bipolarons in La$_2$CuO$_4$

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Abstract. We present calculations of the binding energies of peroxy (O_2^{2-}) bipolarons in La$_2$CuO$_4$. Our results strongly suggest that these species are weakly bound with respect to isolated hole species. Estimates of the effective mass of the bipolaronic species based on our calculated relaxed geometries are consistent with experimental observation for the superconducting state of the material.

There has been extensive recent debate on the possible rôle of bipolarons in high-temperature superconductors [1–7]. In particular, it has been argued that the superconducting state of cuprate superconductors can be envisaged in terms of a Bose condensation of such species. There is, however, considerable speculation and uncertainty concerning the nature of bipolarons in these materials. Several studies both theoretical and experimental [8–13] have established that the hole species in cuprates are predominantly O(2p) in character. A simple model for the bipolaron therefore places two holes on nearest-neighbour oxygen sites, thereby generating a localized state corresponding to the O_2^{2-} peroxy anion, for which owing to the axial, Jahn–Teller distortion of the CuO$_6$ octahedron in La$_2$CuO$_4$ and other cuprates, two structures are possible: the equatorial–equatorial (ee) and axial–equatorial (ae) configurations shown in figure 1. We note that there is evidence [14] that the polaronic state in superconducting cuprates is a Zhang–Rice singlet [15] in which the hole is distributed over four in-plane oxygen sites. We might therefore propose models for the bipolaron that are more complex than that considered here. Our model is, however, a plausible candidate for a small-bipolaron structure, which, moreover, allows us readily to explore the interaction of bipolarons with the surrounding lattice—a key factor in considering their mobility.

Earlier computer modelling studies of ourselves [16, 17], and of Allan and Mackrodt [18] have established the stability of such bipolarons in both La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_7$, for which our calculations suggested small binding energies of ∼0–0.1 eV. The present letter will first refine and extend these studies; but more importantly we will present detailed models for the relaxed geometry of peroxy bipolarons in La$_2$CuO$_4$ which have not been reported previously. The estimated effective masses of the bipolarons based on our calculated geometries are consistent with those observed in the superconducting state of La$_2$CuO$_4$.

We use the same procedures as in our previous studies [16, 17], which model both the simple hole and the peroxy anion as a substitutional defect embedded in the La$_2$CuO$_4$ structure. Interatomic potentials are used to represent all interactions involving the hole,

the peroxy anion and the host lattice ions, as discussed in greater detail below. Using these potentials, we then relax the hole and peroxy species and a large region of surrounding lattice ions (containing ~600 ions) until all ions are at zero force. The polarization of the more distant regions of the crystal may then be calculated using the simple approach originally formulated by Mott and Littleton [19]. The present calculation employed the CASCADE code [20].

A large number of studies, reviewed recently by Harding [21], have demonstrated the reliability of these procedures for yielding *quantitative* estimates of defect formation energies and for modelling accurately the local relaxed structure around defects and substitutionals. The methods have also been extensively and successfully applied to modelling defects and dopants in high-T_c superconductors; recent applications can be found in references [22–25].

An alternative approach to the present problem is to apply quantum mechanical techniques to clusters representing the defect and surrounding lattice. The simpler method employed here has, however, in the present context a number of distinct advantages over the use of such techniques. In particular, it allows a far more detailed treatment of lattice relaxation—a crucial consideration in this study. In addition, the calculation of the binding energy of the peroxy bipolaron is simple and straightforward, unlike the case for quantum cluster calculations. Moreover, a number of calculations [26, 27] have shown that 'Mott–Littleton' calculations of the type employed here may accurately reproduce the structures and energies of detailed quantum mechanical calculations. They are therefore the preferred technique for the problems addressed in this letter.

Table 1. Potential parameters for Morse potential for O_2^{2-} ion calculated using *ab initio* methods. Form of potential: $V(r) = D\{1 - \exp[-\beta(r - r_e)]\}^2$.

D/eV	$\beta/\text{Å}^{-1}$	$r_e/\text{Å}$
0.5789	2.3097	1.709

The reliability of the results of our calculations is of course critically dependent on the interatomic potentials used. Here we use the Born, shell-model potentials for La_2CuO_4 derived in our earlier work, whose reliability for modelling the properties of the perfect and defective La_2CuO_4 lattice has been previously shown [16–18]. But the most critical feature of the parametrization in the present study concerns the *intra*molecular potential for the peroxy anion. This is modelled using a Morse function to represent the covalent bond between the two component oxygen atoms. In our earlier study [16, 17], parameters were taken from the *iso*electronic F_2 molecule. In view of the importance of high accuracy for these parameters, the present study uses a parametrization derived from a high-level quantum mechanical calculation of the energy of the O_2^{2-} ion as a function of bond length. These calculations employed Hartree–Fock techniques with TZVP basis sets and MP4 correlation corrections. Energies were calculated for 12 points with bond lengths ranging from 1.52 Å to 1.78 Å, with resulting potential energy surfaces being fitted to the Morse function. The resulting parameters are reported in table 1. All other potential parameters are as in our previous study [16, 17].

The calculated energies for the single-hole species (modelled as an O^- ion), and the two configurations of the peroxy bipolarons are reported in table 2; and the resulting calculated binding energies of the peroxy anions with respect to component holes are given in table 3. We find, as in our previous study, that both bipolaron configurations are bound, with the 'ae' configuration shown in figure 1(b) having a slightly greater binding energy. The
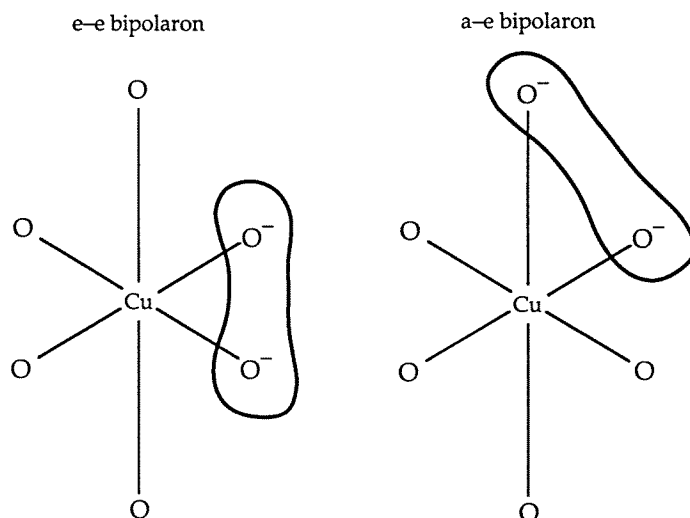
Figure 1. Equatorial–equatorial (ee) and axial–equatorial (ae) configurations of the peroxy bipolarons.

Table 2. Calculated energies for hole and bipolaron species.

Species	Energy* (eV)
Axial hole (O$^-$)	14.70
Equatorial hole (O$^-$)	14.19
'ae' bipolaron (O$_2^{2-}$)	28.75
'ee' bipolaron (O$_2^{2-}$)	28.32

* The calculated energy relates to the process of replacing lattice O^{2-} ions by O$^-$ and O$_2^{2-}$ species and does not include the ionization energy required to create hole species.

**Table 3.** Calculated binding energies of the peroxy bipolaron with respect to isolated species.

Bipolaron	Energy (eV)
'ee'	0.06
'ae'	0.14

binding energies are a little higher than those calculated previously, and we consider the present results to be more reliable owing to the improved parametrization of the peroxy *intra*molecular potential and the use of appreciably larger explicitly relaxed regions in the defect calculations. Some caution must, however, be exercised in interpreting these results. The binding energies are small compared with the total energies of the bipolaronic 'defects', and the relative energies of the configurations may be sensitive to the potential parameters. Nevertheless, the most important qualitative feature of the results, namely that the peroxy bipolaron is weakly bound—a result obtained in our previous work and reinforced in the present study—is, we consider, reliable.

Turning now to the structures of the two bipolarons, table 4 reports the calculated displacements of the component oxygen ions within the relaxed peroxy species. The nature

Table 4. Calculated displacements of oxygen ions within peroxy bipolarons.

Oxygen site	Displacement/Å
Equatorial oxygen in 'ee' bipolaron	0.24
Equatorial oxygen in 'ae' bipolaron	0.06
Axial oxygen in 'ae' bipolaron	0.28
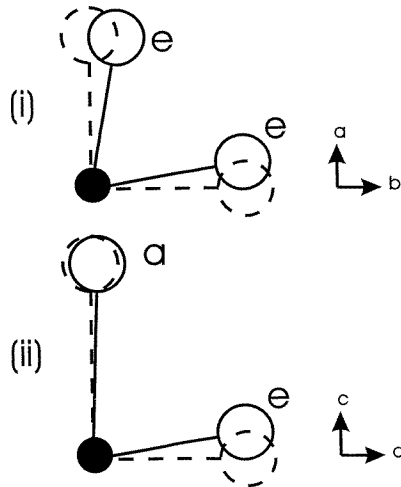
Figure 2. The relaxed configuration of (i) 'ee' and (ii) the 'ae' bipolarons. The dashed lines indicate the unrelaxed lattice sites. Open circles represent the component O^- ions of the bipolaron; the full circle represents the central Cu^{2+} ion in each case.

of the relaxations is indicated diagrammatically in figure 2. We note that the ions displace in an 'inwards' direction by ∼0.14–0.2 Å owing to the covalent bonds of the peroxy anion. The surrounding lattice ion displacements are of the same order for nearest-neighbour metal and oxygen ions.

Let us now consider the consequences of these calculated structures for the possible rôle of these bipolarons as charge carriers in the superconducting state of La_2CuO_4. One of the most persuasive arguments *against* bipolaronic models of superconductivity is that the lattice relaxation required to stabilize the bipolaron would require a thermally activated migration mechanism for transport of this charge carrier; or alternatively (and equivalently) the effective mass of the bipolaron would be too great to permit it to act as the carrier in the superconducting state. We have therefore used our calculated relaxed structure of the bipolaron to estimate the effective mass.

In the Holstein model of polaron formation [28], the effective mass ratio is given by the simple relationship:

$$m^*/m = \exp([x/u])^2 \qquad (1)$$

where $u = (2\hbar/M\omega)^{1/2}$ is the amplitude of the zero-point motions and x is the stabilizing displacement of the polaron. Using the value $\omega \approx 50$ meV suggested by infrared and neutron data [29, 30], together with the oxygen mass, gives $u \approx 0.1$ Å. If we now take the average of the calculated displacements of the oxygen atoms in the more stable 'ae' bipolaron (for which our calculations give a value of ∼0.17 Å) together with this estimate

of u, then from equation (1) we obtain for the mass enhancement:

$$m^*/m \sim 18.$$

This estimate is, of course, very approximate; moreover, it is known that the Holstein model exaggerates the mass enhancement. However, the value calculated for m^*/m is within the range of the experimental estimate of ~ 20 [31]. It appears, therefore, that the calculated effective mass is consistent with that observed, suggesting that the relaxations required to stabilize the bipolaron are *not* sufficient to prevent it from acting as an effective charge carrier in superconducting La_2CuO_4. We note that models for the bipolaron structures based on a more delocalized hole distribution would be expected to give rise to less lattice relaxation and therefore a lower effective mass for the species.

The calculations reported in this letter confirm the important conclusion of our previous study regarding the weak but favourable binding of peroxy bipolarons with the suggestion that the axial–equatorial configuration in figure 1(b) is marginally more stable. The relaxations required to stabilize the bipolarons are consistent with the observed effective masses of the charge carrier in the superconducting state. Of course, the real bipolaronic structures will be more complex than the models described here, and factors arising from magnetic terms will contribute to their stability. Our results do, however, strongly suggest that peroxy-like bipolarons will be stable species in cuprate superconductors, and that the stabilizing lattice relaxations will not prevent them from acting as charge carriers.

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