Hole-pairing mechanisms in La_2CuO_4

1988 J. Phys. C: Solid State Phys. 21 L1085

(http://iopscience.iop.org/0022-3719/21/33/003)

J. Phys. C: Solid State Phys. **21** (1988) L1085–L1090. Printed in the UK

LETTER TO THE EDITOR

Hole-pairing mechanisms in La_2CuO_4

C R A Catlow†, S M Tomlinson†, M S Islam‡ and M Leslie§
† Department of Chemistry, University of Keele, Staffs ST5 5BG, UK
‡ Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
§ SERC Daresbury Laboratory, Warrington WA4 4AD, UK

Received 7 July 1988

Abstract. We consider various possible hole-coupling mechanisms in the high-T_c superconductor, doped La_2CuO_4. Negative-U processes are energetically unfavourable. It is possible that bipolaronic species may be stabilised when antiferromagnetic energies and coupling terms arising from the distortions of the CuO_6 octahedra are taken into account.

It has become increasingly clear that before a proper understanding can be acquired of the recently discovered high-T_c superconductors (Bednorz and Müller 1986, Wu *et al* 1987) it will be necessary to provide a detailed mechanism for the hole-pairing process. Several recent studies have shown that the coherence length of the hole pairs in the high-T_c materials is short (approximately 5–10 Å (see for example Kastner *et al* 1988)) and in this Letter we explore various possibilities, in chemical terms, for such pair species. Our discussion is supported by estimates of lattice and polarisation energy terms obtained using simulation methods described in a previous paper (Islam *et al* 1988). We concentrate on the case of the doped La_2CuO_4 material; but our arguments have general implications for high-T_c materials.

Doped superconducting La_2CuO_4 contains divalent ions substituting for the La^{3+} host cations with charge compensation by hole formation. The question of whether such holes are predominatly in Cu(3d) or O(2p) bands remains controversial. Several spectroscopic studies have suggested that the hole states are predominantly formed from O(2p) orbitals. In contrast, EXAFS studies (Alp *et al* 1987, Saito *et al* 1987) have suggested that there is variable valence on the Cu sublattice. It is almost certain that the hole state will have both Cu(3d) and O(2p) character. Our earlier calculations (Islam *et al* 1988) favour the formation of distinct Cu^{3+} ions; but we note that there are uncertainties in our estimates of the relative energies of Cu^{3+} and O^- species, owing to uncertainties in the free-ion terms that must be added to our calculated energies. Our concern here is to understand how hole species on both sublattices might pair; for this task our calculation procedures are well suited as they model accurately the Coulomb and polarisation energies, which are the predominant terms in any localised coupling process.

We will now consider various pairing mechanisms.

Charge disproportionation (or negative-U) behaviour in the Cu(3d) bands. A number of mechanisms can be examined.

0022-3719/88/331085 + 06 $02.50

(i) Cu^{2+} disproportionation, i.e. the reaction:

$$2Cu^{2+} \rightarrow Cu^{3+} + Cu^{+}. \tag{1}$$

We note that Wilson (1987, 1988) has argued that 'charge fluctuations' related to Cu(3d) negative-U processes may be important.

(ii) Cu^{3+} disproportionation; that is

$$2Cu^{3+} \rightarrow Cu^{4+} + Cu^{2+}. \tag{2}$$

This process seems unlikely as it would create the Cu(IV) valence state, which is unknown in an oxide environment. It would also be unlikely to lead to a suitable spin configuration. Nevertheless, in view of the frequent occurrence of unusual valence states in perovskite-like compounds, it should be investigated.

Charge disproportionation (or negative-U) on the oxygen sublattice where we consider the pairing energy of holes on the oxygen sublattice, which may be written in simple terms as:

$$O^{-} + O^{-} \rightarrow O^{2-} + O^{0}. \tag{3}$$

Peroxy ion formation in which O^{-} ions on neighbouring species couple to form a peroxy O_2^{2-}-like species, i.e. an oxygen hole bipolaron.

Bipolaron formation of Cu(3d) holes in which pairs of holes on neighbouring Cu sites are bound by their mutual polarisation field.

Antiferromagnetically stabilised Cu(3d) bipolarons in which the antiferromagnetic coupling energy leads to an additional stabilisation energy for the bipolaron as discussed in detail by de Jongh (1988).

Antiferromagnetically and elastically coupled bipolarons in which the bipolaron is stabilised by additional terms arising from the elastic strain energy due to the change in the geometry of the CuO_6 octahedron consequent upon forming a d^8 ion.

In attempting to assess the stability of the above species, we use the same simulation techniques with the same inter-atomic potentials for La_2CuO_4 as in our previous study (Islam *et al* 1988). We treat holes on the Cu and O sublattices as Cu^{3+} and O^{-} polaron species respectively. It was necessary to derive potential parameters for the Cu^{4+}–O^{2-} interaction. This was achieved by semi-empirical procedures employing electron gas techniques (as was done for the Cu^{3+}–O^{2-} interaction in our previous study). The parameters, which are not reported elsewhere, are tabulated in table 1.

Our modelling techniques allow us to obtain good estimates of the polarisation energy of the surrounding lattice. This may be done in two ways: firstly, the 'thermal' polarisation energy may be calculated by allowing both nuclear and electronic relaxation

Table 1. Potential parameters used in the present study not reported by Islam *et al* (1988).

Born–Mayer function			
Interaction	A (eV)	ρ (Å)	
Cu^{4+}–O^{2-}	1048.21	0.31867	
Morse function			
Interaction	D_e (eV)	β ($Å^{-1}$)	r (Å)
O^{-}–O^{-}	1.64065	2.911	1.435

(core and shell relaxation in the shell-model (Dick and Overhauser 1958) treatment used in our calculations); secondly, the 'optical' polarisation energy may be calculated, in which only electronic (i.e. shell) relaxation is allowed.

De Jongh (1988) has argued that 'small bipolarons' which are stabilised by nuclear relaxation may be responsible for superconductivity. He suggests that the tunnelling migration rates of bipolarons may be less than the frequencies of the soft phonon modes in high-T_c materials (Birgeneau *et al* 1987, Islam *et al* 1988). The latter soft modes may, therefore, assist the migration of the bipolaron.

In our treatment of the peroxy bipolaron, an attractive Morse function was allowed to act between the component O^- ions. The parameters, which were taken from data for the isostructural F_2 molecule, are given in table 1. Two configurations were considered. In the first, both O^- ions were located at nearest-neighbour equatorial sites. In the second, one O^- ion was at an equatorial site, while the other was located at a nearest-neighbour axial site.

For the Cu^{3+} bipolarons, we also considered two configurations: a nearest-neighbour pair of Cu^{3+} ions separated by a bridging oxygen (see figure 1) and a pair in which the

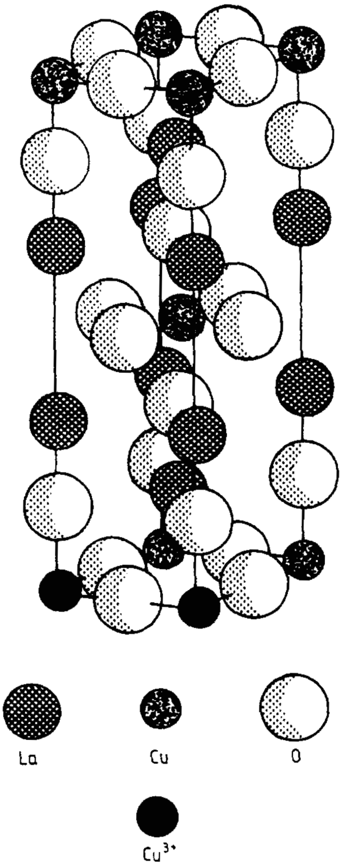

Figure 1. The intra-layer bipolaron (configuration 1) (based on figure given by Yu *et al* (1987)).

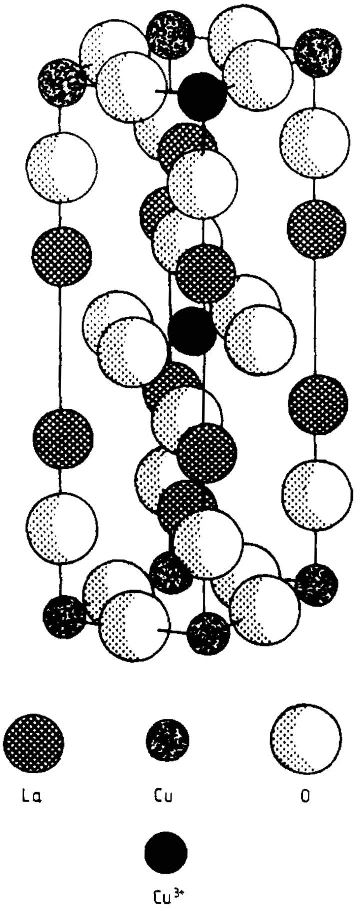

Figure 2. The inter-layer bipolaron (configuration 2) (based on figure given by Yu *et al* (1987)).

two Cu^{3+} ions are in different layers (see figure 2) with the shortest possible Cu–Cu distance. We refer to the former as an intra-layer bipolaron and to the latter as an inter-layer bipolaron.

Our calculated energies for reactions (1)–(3) and the peroxy and Cu(3d) bipolaron formation energies are given in table 2, where our sign convention is such that a positive sign indicates an energetically unfavourable process.

Table 2.

Reaction† of process	Energy (eV)	
	Thermal	Optical
Reaction 1 } Cu ‘U’-energies	4.20	9.59
Reaction 2	4.38	9.84
Reaction 3 O ‘U’-energy	1.29	7.00
Peroxy formation‡		
Equatorial–equatorial	−0.23	2.94
Equational–axial	−0.04	2.43
Cu^{3+} bipolaron formation‡		
Intra-layer (figure 1)	0.46	2.07
Inter-layer (figure 2)	0.04	0.92
Antiferromagnetic coupling Energy§	−0.05 → −0.1	

† For details of reactions see text.

‡ Energies are given with respect to isolated component hole states (O^- or Cu^{3+}).

§ Aharony *et al* 1988, de Jongh 1988.

It is immediately clear that the conventional negative-U process in both the Cu(3d) and O(2p) bands can be ruled out. The energies of reactions (1)–(3) are large and positive. We note that a detailed discussion of negative-U models has been given by Wilson (1987, 1988). He proposes that Cu^{3+} holes cause charge fluctuations resulting in electron pairing. Our calculated energies do not support these models. Our calculation of positive Hubbard U-values accords, however, with the results of band-theory calculations.

We do find appreciable stability for one of the ‘peroxy’ types of bipolaron species, which is bound by approximately 0.2 eV. The formation of such species might be expected if holes are predominantly localised on the oxygen sublattice. However, we should add that there is some uncertainty in the calculated pairing energy of this species, arising from the choice of covalent bonding parameters.

When we examine the Cu(3d) bipolaron, the energy is unfavourable for the intra-layer configuration (figure 1), as indeed was the case for all configurations reported in our earlier study (Islam *et al* 1988); although the polarisation energy is again favourable by about 3 eV. However, for the nearest-neighbour bipolaron, magnetic terms will provide an additional energy favouring their formation as argued in detail by de Jongh (1988). For, on forming a Cu^{3+} hole state, the antiferromagnetic super-exchange coupling between the copper atoms on which the hole is localised and the surrounding Cu atoms is broken due to the removal of the unpaired spin. However, on forming the nearest-neighbour bipolaron, the total number of broken Cu–Cu antiferromagnetic couplings is reduced by one, i.e. we should gain an energy approximately equal to the magnitude of this term, which has been estimated to lie in the range 0.05–0.1 eV (see de Jongh 1988). This would be insufficient to stablise the intra-layer bipolaron.

In contrast to configuration (1), the inter-layer bipolaron is only slightly unbound by ≃0.04 eV. This is sufficiently small for magnetic terms to lead to its stabilisation, although such effects would be expected to be less significant for this more widely separated bipolaron. However, it is possible that there is an additional elastic energy term that will assist the coupling process. We would expect there to be an elastic strain field associated with a single Cu^{3+} small polaron. On forming this species from the d^9Cu^{2+} ion, an electron is removed from the $d_{(x^2-y^2)}$ orbital in the equatorial plane of the tetragonally distorted CuO_6 octahedron; this will enhance the distortion with the equatorial oxygens moving inwards and the axial Cu–O bonds elongating. Coupling of the elastic strain fields of the Cu^{3+} polaron could, therefore, assist the stabilisation of the bipolaron. Preliminary calculations in which a 10% additional axial elongation was imposed on the $Cu^{3+}O_6$ octahedron did not yield a more favourable binding energy. In view of the lack of any stereo-chemical data on the extent of this distortion, detailed calculations are not at present useful. It remains plausible that the coupling mechanism will contribute to bipolaron stability.

Our results thus support inter-layer bipolaron models (of the type shown in figure 2) for superconductivity in doped La_2CuO_4. We suggest that bipolaron stability may require three factors: (i) large polarisation energies, which are in turn associated with materials with high dielectric constants; (ii) an antiferromagnetic coupling energy; and (iii) the elastic strain interaction due to the change in electron configuration on forming the Cu^{3+} hole. In addition, soft phonon modes are needed to assist the propagation of the bipolaron. Clearly this propagation needs a continuous structure for the Cu–O sublattice, i.e. Cu–O chains would be the minimum requirement for bipolaron mobility. Moreover, since the bipolaron motion is phonon-assisted, an isotope effect on T_c would be expected, and is observed (Batlogg *et al* 1987). It is clear from this discussion that high-T_c behaviour requires a coincidence of several factors in the same material, which is consistent with the rarity of the effect.

It is also evident from our calculations that the binding energy for bipolarons will be small (i.e. <0.1 eV). Such species would, therefore, dissociate at low temperatures. Higher binding energies might be expected to lead to higher values of T_c. However, more strongly bound species would be associated with larger distortions of the surrounding lattice and their motion would be activated.

We should recall at this point that our calculations found stability for the peroxy bipolaron. We would suggest, therefore, that if the hole states have predominantly O(2p) character, such species provide plausible models for the hole-pairing mechanism. If, however, the holes are predominantly Cu(3d) in character the bipolaron shown in figure 2 is the most likely model.

In concluding, we note that our models are not incompatible with other theoretical approaches, for example the RVB theories advanced by Anderson and co-workers (Anderson 1987). Our aim has been to provide a more 'chemical' interpretation of the possible bipolaron species, and to account for their stability.

We are grateful to Dr A M Stoneham for several useful discussions.

References

Aharony A, Birgeneau R J, Coniglio A, Kastner M A and Stanley H E 1988 *Phys. Rev. Lett.* **60** 1330

Alp E E, Shenoy G K, Hinks D G, Capone D W II, Soderholm L, Schuttler H-B, Guo J, Ellis D E, Montano P A and Ramanathan M 1987 *Phys. Rev.* B **35** 7199

Anderson P W 1987 *Science* **235** 1196

Batlogg B, Kourouklis G, Weber W, Cava R J, Jayaraman A, White A E, Short K T, Rupp L W and Rietman E A 1987 *Phys. Rev. Lett.* **59** 912

Bednorz J G and Müller K A 1988 *Z. Phys.* B **64** 189

Birgeneau R J, Chen C Y, Gabbe D R, Jenssen H P, Kastner, M A, Peters C J, Picone P J, Thio T, Thurston T R, Tuller H L, Axe J D, Böni P and Shirane G 1987 *Phys. Rev. Lett.* **59** 1329

de Jongh L J 1988 *Physica* C **152** 171

Dick B G and Overhauser A W 1958 *Phys. Rev.* **112** 90

Islam M S, Leslie M, Tomlinson S M and Catlow C R A 1988 *J. Phys. C: Solid State Phys.* **21** L109

Kastner M A, Birgeneau R J, Chen C Y, Chiang Y M, Gabbe D R, Jenssen H P, Junk T, Peters C J, Picone P J, Thio T, Thurston T R and Tuller H L 1988 *Phys. Rev.* B **37** 111

Saito Y, Noji T, Hirokawa K, Endo A, Maisuzaki N, Katsumata M and Higuchi N 1987 *Japan. J. Appl. Phys.* **26** L838

Wilson J A 1987 *J. Phys. C: Solid State Phys.* **20** L911

—— 1988 *J. Phys. C: Solid State Phys.* **21** 2067

Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908

Yu J, Freeman A J and Xu J H 1987 *Phys. Rev. Lett.* **58** 1035