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1989 J. Phys.: Condens. Matter 1 9051

(http://iopscience.iop.org/0953-8984/1/45/028)

J. Phys.: Condens. Matter 1 (1989) 9051–9055. Printed in the UK

LETTER TO THE EDITOR

# The role of off-plane oxygens in the enhancement of the pairing interaction in Cu–O clusters

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Received 16 August 1989

**Abstract.** The influence of apex oxygens on the pairing interaction between the holes in Cu–O clusters has been investigated by using an exact diagonalisation method. A model Hamiltonian consisting of on-site and nearest-neighbour Coulomb repulsion terms is defined for 9-site planar and 11-site Cu–O clusters having two additional O atoms on the top of Cu-sites. The results indicate that these apex oxygens may play a significant role in enhancing pairing in two-dimensional Cu–O planes.

During last two years or so extensive investigations have been carried out to obtain an understanding of the basic mechanism of pairing in high-$T_c$ superconductors. It is generally believed that the pairing mechanism is not the traditional phonon-mediated one. Although a number of mechanisms involving either spin degrees of freedom or other electronic-charge degrees of freedom have been proposed [1–5], there is no agreement about the nature of pairing in high-$T_c$ materials.

Almost all the proposals concerning the pairing mechanism involve two-dimensional Cu–O planes and model Hamiltonians of the Hubbard-type or their extensions to include Cu–O sites explicitly. However, it is known that $T_c$ increases with increasing number of superconducting $CuO_2$ layers per block. This results in the $T_c$ of triple Pervoskite structures and Aurivillus-like structures being larger than $La_2CuO_4$ type structures. In addition it is observed [6, 7] that, for the same number of copper layers, $T_c$ is higher in those compounds that have a redox layer than those without, e.g. $La_2CaO_4$ as compared with $Ti_2Ba_2CuO_6$ or $Bi_2Sr_2CuO_6$. In fact all materials having $T_c > 40$ K have a redox layer present, irrespective of the number of $CuO_2$ layers existing in the block. Such a redox layer is connected to $CuO_2$ plane by an oxygen bridge. The present work, motivated by these observations, investigates the role of off-plane apex oxygens in enhancing the pairing tendancies in Cu–O planes.

In order to examine the role of apex oxygens, we have carried out exact diagonalisation studies on small Cu–O clusters. Such an approach has been used by a number of workers [8, 9] for a variety of problems and has given valuable insight.

Recently, Hirsch and co-workers [10, 11] have investigated 8-, 9-, 12- and 16-site Cu–O clusters, all with planar geometry. Their work indicates that the stable two-hole pairing is possible for a range of parameters and that both spin and charge degrees of freedom can give rise to pairing. A similar calculation has been reported by Jones and Managham [12] on a $Cu_4O_8$ cluster in a ring geometry and they have found an effective attractive interaction for hole pairs. The present work is in the same spirit but with an

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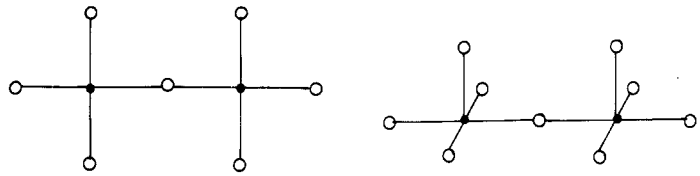

**Figure 1.** Geometry of the 9- and 11-site clusters: full circles, Cu; open circles, O.

important difference. We have investigated 9- and 11-site clusters as shown in figure 1. The 11-site cluster has two apex oxygens interacting with the plane. The emphasis in the present work is on the role of these apex oxygen atoms, which turns out to be very significant.

The model Hamiltonian for these cluster is defined as

$$H = t\sum_{i,l,\sigma}(d^+_{i\sigma}b_{l\sigma} + \text{HC}) + \varepsilon\sum_{l,\sigma} b^+_{l\sigma}b_{l\sigma} + U\sum_i n_{i\uparrow}n_{i\downarrow} + U_p\sum_l n_{l\uparrow}n_{l\downarrow}$$
$$+ V\sum_{i,l} n_i n_l + t'\sum_{i,\alpha,\sigma}(d^+_{i\sigma}c_{\alpha\sigma} + \text{HC}) + U'_p\sum_\alpha n_{\alpha\uparrow}n_{\alpha\downarrow}$$
$$+ \varepsilon\sum_{\alpha,\sigma} c^+_{\alpha\sigma}c_{\alpha\sigma} \tag{1}$$

where $d^+_{i\sigma}$, $b^+_{l\sigma}$ are creation operators for electrons on Cu and oxygen (in-plane) sites respectively, $\varepsilon$ is the single-particle level for oxygen, $U$ and $U_p$ are Hubbard repulsions on Cu and O (in-plane) sites and $V$ the intersite nearest-neighbour repulsion between Cu–O (in-plane). The last three terms are operative only in the case of 11-site clusters. Here, $t'$ is the hopping term for Cu and off-plane oxygen and $U'_p$ is the Hubbard repulsion for off-plane oxygen. $c^+_\alpha$ refers to the creation operator for off-plane oxygen. It is reasonable to expect $t > t'$ and $U_p \neq U_{p'}$ in general. The effects of varying these terms are discussed below.

The calculations are carried out by direct diagonalisation in the sub-space of $S_z$. The reference state is taken to be one hole per copper site. The pairing tendencies are examined by calculating one- and two-hole binding energies. Then, the two-hole pairing is favoured if $\Delta$, which is defined as

$$\Delta = \Delta E(2h) - 2\Delta E(1h) \tag{2}$$

is negative, where

$$\Delta E(nh) = E(N-n) - E(N) \tag{3}$$

where $E(N)$ is the ground-state energy of an $N$-electron system.

Before we discuss the present results concerning the effects of apex oxygens we summarise the conclusions drawn by Hirsch and co-workers [11] based on their planar cluster studies. They found that the 9-site planar cluster does not show an attractive pairing interaction unless the inter-site copper–oxygen repulsion $V$ is greater than about 3. Furthermore, such a pairing becomes stable only in the small range of inter-site O–O repulsion ($V_{OO}$), not included in the present calculation. All other clusters, that is 8, 12 and 16 sites, show stable pairing for a reasonable range of parameters, the pairing being strongest for 12-site clusters. Our choice of parameters is thus guided by these calculations. We have chosen $U = 10$, $U_p = 2$, $t' = 0.2$. Our results for 9-site clusters

**Table 1.** Values of Δ for different values of $U'_p$ for 11-site cluster in units of $t$.

| $V$ | $u'_p$ | $\Delta H$(1h) | $\Delta E$(2h) | Δ |
|---|---|---|---|---|
| | 0.0 | −4.3868 | −8.3174 | 0.4562 |
| | 0.5 | −4.7507 | −10.7663 | −1.2649 |
| 0 | 1.0 | −5.1291 | −13.2105 | −2.9524 |
| | 1.5 | −5.5201 | −15.6504 | −4.6101 |
| | 2.0 | −5.9221 | −18.0869 | −6.2426 |
| | 0.0 | −16.5735 | −32.9086 | 0.2384 |
| | 0.5 | −16.6017 | −35.3982 | −2.1948 |
| 2 | 1.0 | −16.6324 | −37.8872 | −4.6224 |
| | 1.5 | −16.6660 | −40.3756 | −7.0435 |
| | 2.0 | −16.7029 | −42.8633 | −9.4574 |

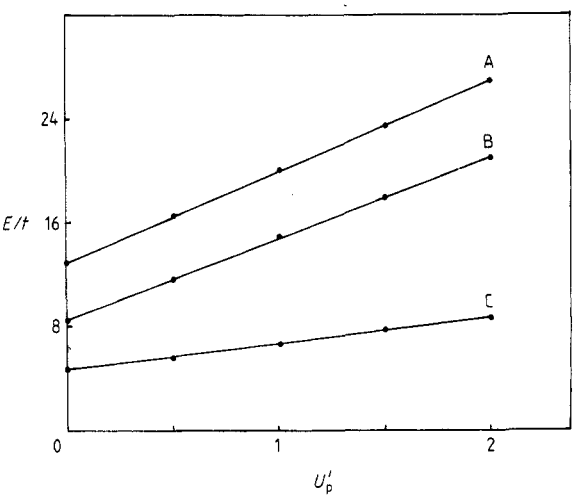


**Figure 2.** Total energy as a function of $U$ for an 11-site cluster. Other parameters are: $V = 0$, $t' = 0.2$, $=0$. A, reference state; B, one-hole state; C, two-hole state.

with these parameters are identical to the ones reported by Hirsch *et al* [11] and show no attractive pairing.

We now present our results for an 11-site cluster. We have investigated the pairing tendencies by varying $U_{p'}$ and $t'$. The results for 0-, 1- and 2-hole states for the 1-hole binding energies, 2-hole binding energies and Δ for $V = 0$ and 2 are presented in table 1. The behaviour of the total energy as a function of $U'_p$ is shown in figure 2. We have also calculated spin correlation functions between Cu sites, defined as $\frac{1}{4}\langle(n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow})\rangle$, and these are shown in table 2. The striking feature of the result is the drastic reduction in Δ, making the pairing interactions very highly attractive for all values of $U'_p$ except $U'_p = 0$. Examination of table 1 and figure 1 gives the following picture. The undoped system, comprising 20 electrons and corresponding to one hole per Cu site, shows the expected strong antiferromagnetic interactions between two Cu sites, the O sites being completely filled. When one hole is introduced into this reference state, the hole goes predominantly on to the O sites in the plane and there is a reduction

**Table 2.** Spin correlation function for 0-, 1- and 2-hole states for an 11-site cluster between the Cu-sites (for $V = 0$).

| $U'_p$ | 0-hole | 1-hole | 2-hole |
|---|---|---|---|
| 0.0 | −0.22 | 0.025 | 0.001 |
| 0.5 | −0.219 | 0.014 | 0.001 |
| 1.0 | −0.215 | 0.014 | 0.001 |
| 1.5 | −0.211 | 0.013 | 0.001 |
| 2.0 | −0.206 | 0.012 | 0.001 |

in the antiferromagnetic spin order (table 2). The apex oxygens are still completely filled at this stage. This is reflected in the rapid increase in the total energy of the one-hole case as a function of $U'_p$. When the second hole is introduced into the system, for the case of $U_p > U'_p$ both holes go predominantly onto O sites in the plane. There is a further decrease in the spin orders: in addition, a small number of holes are also introduced onto the apex oxygens. It is worth noting that, as $U'_p$ increases, the rate of increase of the total energy for two holes is significantly smaller than the corresponding one-hole energies, indicating that the second hole requires far less energy to fit into the already spin-disordered state. This effect is absent in 9-site planar geometry. We have also varied the inter-site repulsion $V$ from 0 to 4. Although for this case the $\Delta$ is strongly negative, as $V$ increases the additional holes predominantly go onto Cu sites and, for $V = 4$, all the holes become localised on Cu sites only. We have also calculated the extended singlet pairing correlations (SPX) having the form [13]

$$c_{i\uparrow}\, c_{i+r\downarrow} - c_{i\downarrow}\, c_{i+r\uparrow}\,. \tag{4}$$

For all cases where $V$ is greater than 0.5 or so, these pairing correlations are zero for all sites, indicating that the singlet pairs relevant to superconductivity are absent. For the case where $V$ is less than 0.5, the dominant pairing correlations are in the plane, holes being on oxygen sites, and are of the order of 0.16.

The effect of varying $t'$ on both $\Delta$ and pairing correlations is found to be small and essentially similar in nature to the one discussed above.

The principal conclusion of our calculations is that the apex oxygens significantly aid and enhance the pairing interactions in the superconducting plane. It is clear that these results are based on the calculations performed on small clusters, and a certain amount of caution is required before they could be generalised. The work of Hirsch and co-workers [11] indicates that the attractive stable pairing was found in 12-site as well as 16-site clusters. Therefore it is quite likely that the enhancement of the pairing due to apex oxygens may be seen in extended systems. Such work is in progress and will be published elsewhere.

## Acknowledgments

One of us (DGK) greatly benefitted from a number of discussions with Professor J Callaway. We are happy to acknowledge a number of discussions with Professor A P B Sinha and Dr R E Amritkar. Financial support from the Department of Science and Technology is gratefully acknowledged.

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