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ELECTRONIC STRUCTURE OF THE CuO_X (X=4, 5 AND 6) MODEL CLUSTERS. II. EFFECTS OF THE MADELUNG POTENTIAL

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Abstract Electronic structure of CuO_5 cluster embedded in the Madelung potential based on the $Tl_2Ba_2CaCu_2O_8$ is largely affected by the electrostatic gradient along the c-axis, where the mainly perturbed level is the apex O-Cu bond. The Madelung potential for the model where Tl and Ca are exchanging their sites each other and where some Tl is substituted for Ca site seems to be preferable for stabilizing the electronic states. It is also clarified that the exchange potential between Cu and O is strongly correlated with the overlap population between them.

INTRODUCTION

The existence of two dimensional network of copper oxide (CuO_2) is essential for the superconductivity in cuprates. Superconductive properties can be affected by parameters such as coordination numbers of O atom to Cu atom, carrier concentration, lattice constants, and the substitution of atoms around the CuO_2 layers.

We have studied the effect of carrier concentration and that of distance between Cu and O (d_{Cu-O}) on the electronic states of the CuOx clusters (x=4, 5, and 6)[1]. In calculation of model clusters, the role of surrounding oxide layers is considered as follows: (1)Constructing layered structure which stabilizes two dimensional CuO_2 layers with appropriate d_{Cu-O} and (2)controlling the carrier concentration, either electron or hole of the CuO_2 layers. These effects can be brought into the cluster calculation by varying d_{Cu-O} and the charge in the model cluster. We have succeeded with this calculation in describing the characteristic of the cuprate superconductors, such as large covalency and the location of the hole doped orbitals.

However, the electronic structure of compounds with layered structure such as ZnO is largely affected by the electrostatic potential

perpendicular to the layers[2]. Therefore, it is interesting to investigate how the external electrostatic field caused by surrounding oxide layers affects the electronic structure of the CuO_2 plane.

In this paper, the effect of external electrostatic field on the electronic structure of CuO_2 layer is studied by DV-Xα cluster calculation. The cluster is the same as used in the previous work and the Madelung potential is applied as an external electrostatic field. The model for applying the Madelung potential is taken from the $Tl_2Ba_2CaCu_2O_8$ system, the structure of which has been well defined by neutron diffraction[3].

The cuprate superconducting materials are known to be antiferromagnetic in its Cu $3d^9$ and O $2p^6$ states without any hole in the system. Antiferromagnetism in this system is due to the so-called Heisenberg's antiferromagnetism. In this case, superexchange interaction between two Cu atoms bonded in straight line to the same O atom, strongly relates to exchange potential between Cu and O atoms. We have calculated the exchange potential between Cu and O atoms as a function of d_{Cu-O} and the formal charge in Cu for CuO_4 clusters.

MODELS AND CALCULATION METHODS

The cluster models used in this calculation is displayed in Fig. 1. Changes in the exchange potential as a function of d_{Cu-O} has been calculated using CuO_4 cluster. The effect of Madelung potential was examined with CuO_5 cluster. The geometrical structure of CuO_5 cluster was taken from The Tl 2-layer system: 1.928 Å for a-axis and 2.70 Å for c-axis. The formal charge of Cu was varied from +1 to +3, and that for O was fixed at -2 in the calculation.

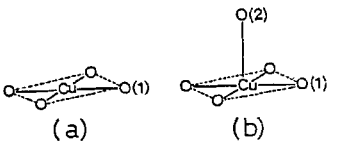

FIGURE 1 (a)CuO_4 and (b)CuO_5 clusters used in this calculation. O(1) is located at the plane site and O(2) is at the apex site.

DV-Xα cluster calculation method is based on the one electron Schrödinger equation where an approximate exchange-correlation interaction of the following expression was used,

$$Exc(\rho) = -3/2\alpha C \int d\vec{r} \rho(\vec{r})^{4/3} \quad (1)$$

where, C is constant and the value α was fixed at 0.7. The basis func-

tion was represented by linear combination of atomic orbitals of Cu 1s to 4p and O 1s to 2p. In calculation with Madelung potential, the point charges were put around the model cluster to represent the electrostatic field in the crystal lattice.

RESULTS AND DISCUSSIONS

In the real system of Tl 2-layer crystal, almost one sixteenth of Tl is substituted for Ca, and a certain part of Tl and Ca are exchanging their site each other as shown in Fig. 2. Figure 3 shows the level structures of CuO_5 clusters for Cu^{+2} state, without any external potentials (a), with external potentials but without substitution (b), and with external potential with substitution (c). With external potential and without the substitution (b), the anomalous level structure were obtained. The bond orbitals between the apex O and Cu are located too low compared to the level structures without external potential (a). When the defects were introduced by substitution of Ca by Tl, the anomaly seems to disappear. Although there are no clear guarantee that the Madelung potential in the real cuprate superconductors is reproduced in this model, it has been shown that the substitution of atoms in the external potential largely affects the level of the apex O and Cu bonds. Madelung potential which gives the minimum total energy should be preferable for the external potential.

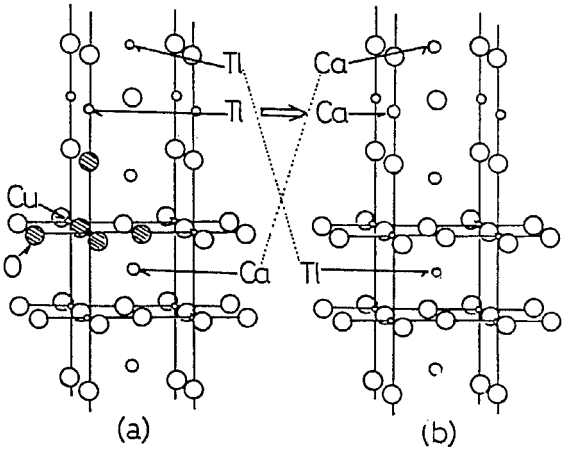

FIGURE 2 Crystal lattice of $Tl_2Ba_2CaCu_2O_8$ in (a)ideal structure without any substitution and (b) real one with substitution. (b): Tl is substituted for Ca as indicated by an arrow. Site exchanging of the Tl and Ca is indicated by dotted line. The shaded Cu and O corresponds to an embedded CuO_5 cluster.

The large covalency of the Cu and O bond is one of the characteristic for the cuprate super-

conductors. The magnitude of covalency calculated overlap population between Cu and O. The dependence of the overlap population for the CuO_4 clusters on the d_{Cu-O} or on the formal charge of Cu is similar to that in the CuO_5 cluster[1]. The value of the overlap population became larger for larger formal charges of Cu. Increasing d_{Cu-O}, the value of the overlap population increases then gradually approaches to zero thorough a maximum value.

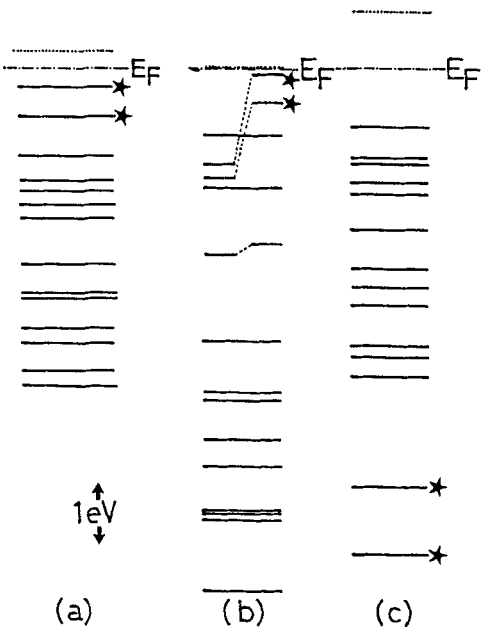

FIGURE 3 DV-Xα $_7$electronic energy levels for the CuO_5^{7-} clusters, (a)without any external potential, (b) with external potential but without substitution, and (c)with external potential with substitution. The levels marked by stars are the bonding orbitals of Cu and apex O.

It is said that the antiferromagnetism feature in its $3d^9$ and O $2p^6$ state is related to the superconductivity of this material. The value of the exchange integral between the unpaired electrons on Cu atoms is directly included in the Hamiltonian considered in the Heisenberg antiferromagnetism. In the present calculation the exchange potential was effectively calculated by eq.(1). Thus direct information on the superexchange interaction between two Cu atoms was obtained. Figure 4 shows the exchange potential for CuO_4 clusters. The exchange potential gives just minimum value at the same d_{Cu-O} where the maximum value is given by the overlap population. Therefore, it is concluded that the exchange potential and the overlap population strongly correlate.

The level structures near the valence levels obtained by DV-Xα cluster calculation for CuO_4 clusters are shown in Fig. 6. The whole level structures drastically changed between Cu^{+1} and Cu^{+2}. This tendency is almost the same as that in CuO_5 cluster[1]. It is known that Tc

takes the maximum value near the formal charge of 2.3 for various cuprate superconductors. The fine changes in the formal charge of Cu between +2 and +3 were represented in Fig. 5(c) and (d), where the changes in the level structures in this region is continuous and hardly any drastic transition was observed.

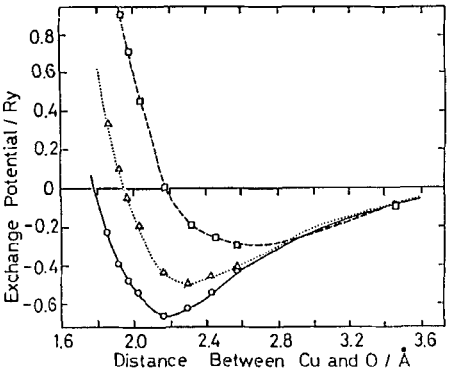

FIGURE 4 The exchange potential between Cu and O atoms for CuO_4 clusters vs. Cu-O bond lengths. The real line indicates CuO_4^{5-} cluster (the formal charge of Cu is +3), the dotted line CuO_4^{6-} (+2) and the broken line CuO_4^{7-} (+1), respectively.

CONCLUSIONS

The substitution of atoms in the external potential largely affected the level of apex O and Cu bonds.

The exchange potential and the overlap population were found to be strongly correlated.

Changes in the level structures of CuO_4 cluster with increasing the valence of Cu from +2 to +3 was continuously.

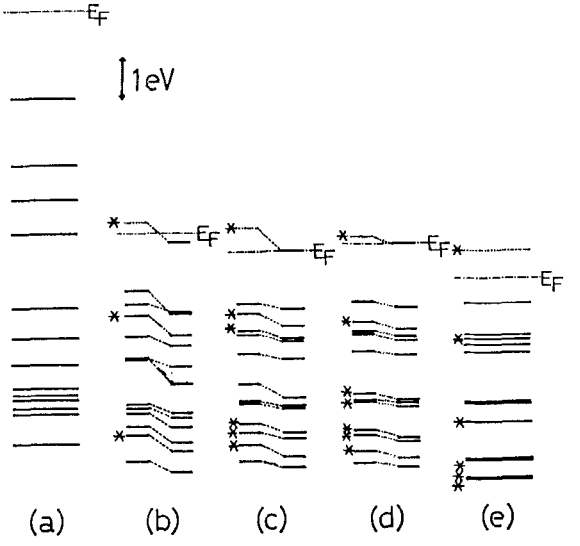

FIGURE 5 DV-Xα electronic energy levels for the CuO_4 clusters. The formal charges of Cu for each cluster are (a)+1, (b)+2, (c)+2.3, (d)+2.5, and (e)+3. E_F is the Fermi level. The levels marked by asterisks have large covalent bonding character.

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