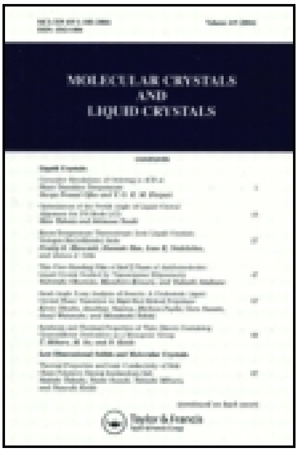

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DV-Xα Calculations of Electronic States and Chemical Bonds in CuO_2-Layered Superconducting Oxides

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DV-Xα CALCULATIONS OF ELECTRONIC STATES AND CHEMICAL BONDS IN CuO_2-LAYERED SUPERCONDUCTING OXIDES

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Abstract DV-Xα cluster calculations for CuO_2-layered superconducting oxides were carried out to investigate the electronic states and chemical bonds. It was suggested that the covalent interaction has a significant role in those compounds to occur superconductivity.

INTRODUCTION

Recently, "n-type" superconductivity was discovered in the $Ln_{2-x}Ce_xCuO_{4-y}$ system (Ln=Pr,Nd,Sm and Eu) for $x=0.15\sim0.18$[1,2]. One wants to understand the role of the covalent interaction between Cu and O in the n-type compounds. Actually, the covalent interaction between Cu and O has been demonstrated by Adachi et al[3,4] to be significant in "p-type" compounds. The characterization of chemical bonds between the elements which form CuO_2-layered oxides is necessary to be made for elucidating the essential features of the crystal structure which may be related to the cause of superconductivity, and for obtaining certain guiding principles for the synthesis of new materials.

The DV-Xα cluster method can provide characteristics of the chemical bonds of various types of cluster models. In the present work, we calculate the electronic structures of four different types of clusters and investigate the covalent interactions of Cu-O, Nd-O and Ce-O in the Nd_2CuO_4-type structure.

CALCULATION METHOD

Figures 1.(A)-(D) show the cluster models used in the calculations which (except for Fig.1 (C)) have structures of the Nd_2CuO_4-type. O(1) and O(2) are oxygens in the CuO_2 plane and in Nd_2O_2 layer, respectively. The interatomic distances for the models given in Fig.1 are set to be the same as those experimentaly obtained for $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ [5]. Those for $CeO_8{}^{12-}$, which has the Oh symmetry were taken from Shanonn's ionic radius[6]. Numerical computations were carried out using the DV-X method[7]. The exchange parameter was fixed at 0.7 throughout the present work. The atomic orbitals of 1s-4p for Cu, 1s-2p for O, 1s-5p for Nd and 1s-6p for Ce were taken into account for the basis functions of LCAO (linear combination of atomic orbitals).

TABLE I. Interatomic distances for four cluster models

Model Cluster(symmetry)	Distance(A)			
$[CuO_{12}]^{22-}$(C4v)	Cu-O(1)	1.97	Cu-O(2)	3.61
$[NdO_8]^{13-}$(C4v)	Nd-O(1)	2.66	Nd-O(2)	2.33
$[CeO_8]^{12-}$(Oh)	Ce-O	2.39		
$[CeO_8]^{12-}$(C4v)	Ce-O(1)	2.66	Ce-O(2)	2.33

RESULTS AND DISCUSSION

1.$[CuO_{12}]^{22-}$ cluster model

The calculated energy levels for a $[CuO_{12}]^{22-}$ cluster are shown in Fig.2 (a). The highest occupied molecular orbital (HOMO) consisted of $Cu3d_{x^2-y^2}$ up-spin orbital and O(1)2p orbital. The lowest occupied molecular orbital (LUMO) consisted of $Cu3d_{x^2-y^2}$ down-spin orbital and O(1)2p orbital. Both orbitals are of $Cu3d_{x^2-y^2}$ - O(1)2p antibonding orbitals. Net charges for individual atoms in the cluster obtained in this calculation are listed in Table II. The deviation of net charge on the Cu atom in the

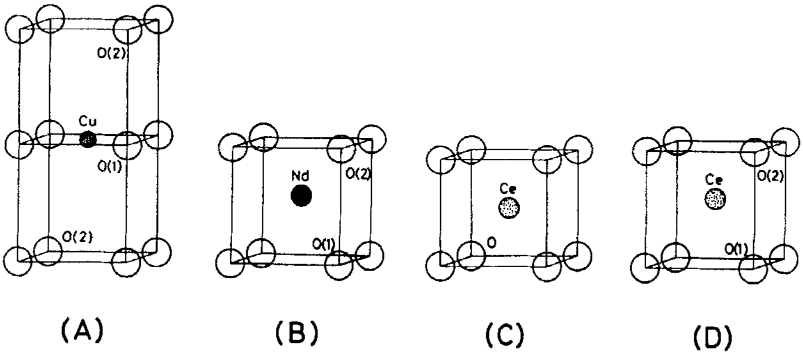

FIGURE 1 Clusters (A:$[CuO_{12}]^{22-}$,B:$[NdO_8]^{13-}$,C:$[CeO_8]^{12-}$ (Oh) and D:$[CeO_8]^{12-}$) used in the present calculations. O(1) is located on the CuO_2 plane site and O(2) is on Nd_2O_2 layer.

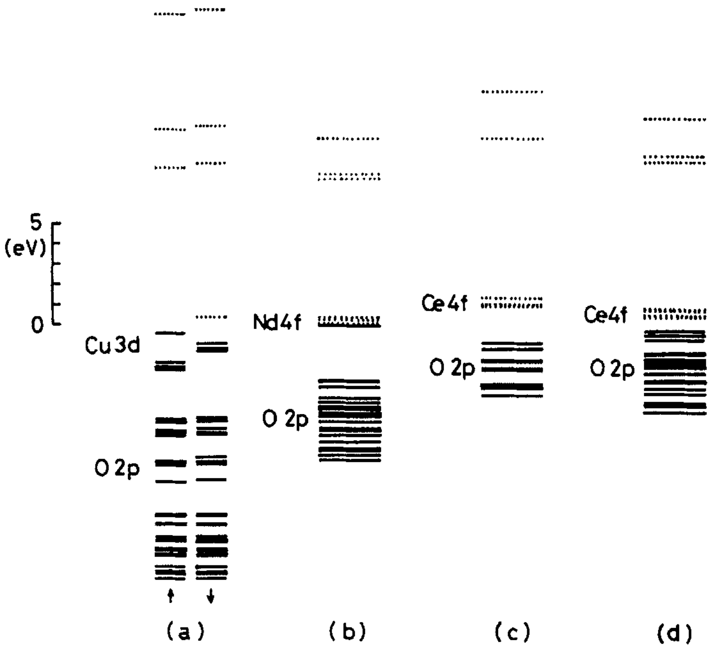

FIGURE 2 DV-Xα electronic energy levels for clusters(a:$[CuO_{12}]^{22-}$,b:$[NdO_8]^{13-}$,c:$[CeO_8]^{12-}$(Oh) and d:$[CeO_8]^{12-}$) in the present calculation.

cluster shown in Fig.1 (A) from the formal charge 2+ indicates that the covalency of the Cu-O(1) bond is significantly strong. On the other hand, the net charge of the O(2) in the same cluster is equal to the formal charge -2.0, and therefore the Cu-O(2) bond is ionic. The energy gap between $Cu3d_{x^2-y^2}$-O2p bonding orbital and $Cu3d_{x^2-y^2}$ -O2p antibonding orbital is relatively small. According to LCAO, it means that the covalent interaction between O and Cu is large compared with that between O and transition metal elements.

2.$[NdO_8]^{13-}$ and $[CeO_8]^{12-}$ cluster models

The calculated energy levels for $[NdO_8]^{13-}$ cluster are shown in Fig.2 (b). Net charges of Nd,O(1) and O(2) are listed in Table II. It is seen that Nd is fairly ionic in this cluster model.

Also for the two $[CeO_8]^{12-}$ clusters shown in Fig.1 (C) and (D) which have O_h and C_{4v} symmetries, respectively, DV-Xα calculations were performed. The distances between Ce and O atoms employed in the present calculation are listed in Table I. The calculated energy levels for these clusters are shown in Fig.2 (c) and (d). Net charges for individual atoms in the clusters are tabulated in Table II. The value of the net charge of a Ce atom in the cluster of the O_h symmetry is nearly equal to the average valence, 3.5+, for Ce in CeO_2 [8]. The energy gap for the O_h-cluster is smaller than that for the C_{4v}-cluster as can be observed in Fig.2 (c) and (d). This result indicates that the covalent interaction between Ce4f orbitals and O2p orbitals is stronger in the C_{4v}-cluster than in the O_h-cluster. For this reason, the net charge for Ce of the C_{4v}-cluster is smaller than that of the O_h-cluster as shown in Table II. Therefore, in the C_{4v}-cluster, a charge transfer may occur from O(2) atom to Ce atom. The Ce^{4+} ions which give electrons to CuO_2 layers would behave electrostatically more or less like Ce^{3+} ions. As a result, it is likely that the regularity of Madelung potential on the Nd_2O_2 layer in $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ would not be significantly disturbed by the substitution of Ce^{4+} for Nd^{3+}.

TABLE II. Net Charges for constituent elements in four different clusters

Model cluster		Net charge	Formal charge
(A) CuO_{12}^{22-}	Cu	1.83	2.00
	O(1)	-1.96	-2.00
	O(2)	-2.00	-2.00
(B) NdO_8^{13-}	Nd	2.71	3.00
	O(1)	-1.96	-2.00
	O(2)	-1.97	-2.00
(C) CeO_8^{12-}(Oh)	Ce	3.13	4.00
(D) CeO_8^{12-}	Ce	2.89	4.00
	O(1)	-1.84	-2.00
	O(2)	-1.88	-2.00

CONCLUSION

DV-Xα calculations for Nd_2CuO_4-type compounds were performed using four different cluster models. A charge transfer between Cu atoms and coordinated oxygen atoms was found to occur in the cluster due to strong covalent interactions. The doped Ce ions were found to play significant roles in $(Nd,Ce)_2CuO_4$.

REFERENCES

1. Y.Tokura, H.Takagi and S.Uchida, Nature 337, 345 (1989).
2. H.Adachi and M.Takano, Physica C 157, 169 (1989).
3. R.Sekine, M.Kawai and H.Adachi, Physica C 159, 161 (1989).
4. F.Izumi, Y.Matsui, H.Takagi, S.Uchida,Y.Tokura and H.Asano, Physica C 158, 433 (1989).
5. R.D.Shannon,Acta Cryst. A32, 751 (1976).
6. H.Adachi,M.Tsukada and C.Satoko,J.Phys.Soc.Jpn. 45, 875 (1978).
7. A.Kotani,H.Mizuta,T.Jo and J.C.Parlebas, Solid State Commun. 53 ,805 (1985).