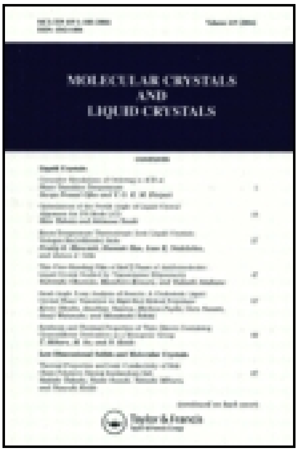

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Theoretical Studies on the Electronic States of Hole-Doped Copper Oxides

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Electronic states of copper oxides were investigated after hole-doping by using Hybrid-DFT (UB2LYP) calculations for three types of model clusters. Energy diagram in hole-doped state is explained by using d-p interaction between $3d_{x^2-y^2}$ orbital of copper and 2p orbital of oxygen and superexchange interaction (SE) between copper orbitals via closed oxygen orbital.

Keywords:Copper oxides, Hole-doping, Density Functional Theory (DFT), CASSCF, Superexchange (SE) interaction, Superconductivity

INTRODUCTION

Since the discovery of high temperature superconductivity in copper oxides such as La_2CuO_4 by Bednorz and Müller in 1986[1], various experiments and calculations have been attempted in order to clarify its mechanism. La_2CuO_4 has the layered perovskite structure consisting of copper, oxygen and lanthanum. In La_2CuO_4, CuO_2 plane and $(LaO)_2$ plane are alternately stacked. Hole is doped in CuO_2 plane after some part of lanthanum is substituted for strontium. High temperature superconductivity is achieved by change of hole-doping concentration. Three shapes of holes were considered by quantum chemical calculations of doped cuprates. One is σ-hole on oxygen by Yamaguchi et al.[2], and the others are two types of π-holes on oxygen by Hirsch and Tang[3] and Goddard III et al.[4]. Photoemission spectroscopy (PES) and Bremsstrahlung isochromat spectroscopy (BIS) made clear that spin singlet state is formed by $3d_{x^2-y^2}$ orbital of copper and p_σ orbital of oxygen by hole-doping[5].

In our previous work[6], *ab initio* calculation about perovskite-type copper oxides before hole-doping was performed in order to elucidate appropriate calculation methods and magnetic interaction between Cu(II) ions. Hartree Fock (HF), Møller Plesset (MP) and hybrid-Density Functional Theory (DFT) methods were executed and spin density, charge density and natural orbital (NO) were obtained for model clusters such as CuOCu (**1**), CuOCuOCu (**2**) and Cu_4O_4 (**3**) as shown in Figure 1. It was found that UB2LYP provided reasonable results compared with experiment in effective exchange integrals (J_{ab}) by using the total energy difference between lowest spin (LS) and highest spin (HS) states[7].

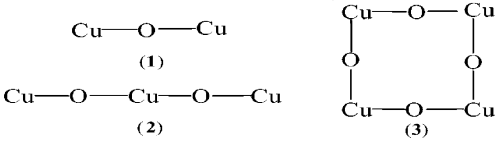


FIGURE 1 Model clusters for computations

In this study, UB2LYP calculations are performed in order to examine the electronic structure and shape of holes for hole-doped **1** - **3**. As three type of holes such as σ-hole ($2p_\sigma$), π-hole ($2p_\pi$) and π⊥-hole ($2p_{\pi\perp}$) are considered, π-hole and π⊥-hole are degenerated for **1** and **2**. Various spin states of σ-hole and π-hole are calculated in order to investigate relative stability between hole-doped LS and HS states. For **1**, three types of spin states are considered (Cu ↓ O ↑ Cu ↑ :LS I, Cu ↑ O ↓ Cu ↑ :LS II, Cu ↑ O ↑ Cu ↑ :HS). For **2**, hole-doped LS (Cu ↑ O↓Cu-↓ O↓Cu ↑) and HS (Cu ↑ O↑Cu ↑ O↑Cu ↑) states are formed by one hole-doping from hole-undoped LS and HS states. CASSCF calculations, which are symmetry-adapted CI computations, are performed for **1** in order to compare the results of UB2LYP calculations.

RESULTS

Tables 1 and 2 show spin density and energy in each spin state of **1** and **2**. σ-hole-doped LS state is more stable than σ-hole-doped HS state because of overlap between $3d_{x^2-y^2}$ orbital of copper and $2p_\sigma$ orbital of oxygen for both **1** and **2**. On the other hand, π-hole-doped HS state is more stable than π-hole-doped LS state because of no overlap between $3d_{x^2-y^2}$ orbital of copper and $2p_\pi$ orbital of oxygen for both **1** and **2**.Figure 2A shows energy gap in each spin state. Though each σ-hole-doped

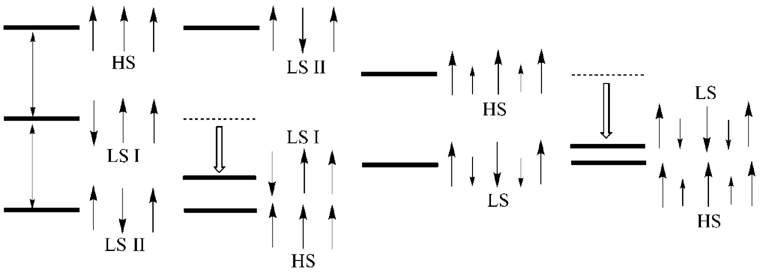
TABLE 1 Spin density in LS and HS states (UB2LYP)

Model			Cu1	O2	Cu3	O4	Cu5
CuOCu	σ-hole	LS I	-0.885	0.873	1.012		
		LS II	0.902	-0.804	0.902		
		HS	1.017	0.967	1.017		
	π-hole	LS I	-0.937	1.031	0.906		
		LS II	0.957	-0.914	0.957		
		HS	0.989	1.142	0.989		
Cu_3O_2	σ-hole	LS	0.849	-0.497	-0.704	-0.497	0.849
		HS	0.957	0.651	0.785	0.651	0.957
	π-hole	LS	0.889	-0.457	-0.864	-0.457	0.889
		HS	0.864	0.691	0.891	0.691	0.864

TABLE 2 Calculated energy(a) and energy gap(a) (UB2LYP)

Model	σ-hole		π-hole	
CuOCu	HS	-3353.4892	LS II	-3353.6440
	LS I	-3353.5156	LS I	-3353.6486
	LS II	-3353.5384	HS	-3353.6490
	ΔHS-LS I	0.0264	ΔLS II-LS I	0.0046
	ΔLS I-LS II	0.0228	ΔLS I-HS	0.0004
Cu_3O_2	HS	-5068.9003	LS	-5069.02631
	LS	-5068.9341	HS	-5069.02633
	ΔHS-LS	0.0338	ΔLS-HS	0.00002

(a) a.u.



σ-hole π-hole σ-hole π-hole

(2A)CuOCu (2B)CuOCuOCu

FIGURE2 Energy diagram for each spin state

state is located at regular interval, π-hole-doped LS II state is very close to π-hole-doped HS state. Figure 2B shows energy diagram in each spin state of **2**. The σ-hole-doped case has larger energy gap than the π-hole-doped case.

Shapes of holes are investigated by the differences of density ρ defined by

$$\Delta\rho=\rho_{\mathrm{before}}-\rho_{\mathrm{after}} \qquad (1)$$

where ρ_{before} and ρ_{after} denote, respectively, density of before and after hole-doping. Hole is formed in the white part, where Δρ is positive. On the other hand, density is increasing in the black part, where Δρ is negative. Figures 3A and 3B show shapes of σ-hole and π-hole for **1** and **2**, respectively. Figure 3C shows shapes of σ-hole, π-hole and π⊥-hole of **3**. Holes are formed on both 2p orbital of oxygen and $3d_{x^2-y^2}$ orbital of copper. It shows that holes are delocalized on both oxygen and copper. In addition to this, there exists the part which has the negative value of Δρ, around holes. This fact suggests that molecular orbitals of each models are changed by hole-doping.

σ-hole π-hole σ-hole π-hole

(3A)CuOCu (3B)CuOCuOCu

σ-hole π-hole π⊥-hole

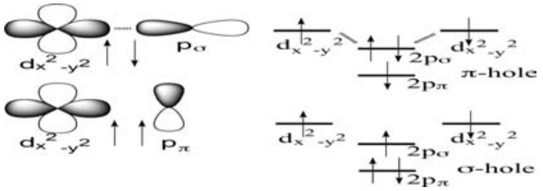
$(3C)Cu_4O_4$

FIGURE3 Shapes of holes

CASSCF calculations for **1** were performed in order to compare the results of hybrid-DFT calculations. Three types of 2p orbitals of oxygen and two $3d_{x^2-y^2}$ orbitals of copper are selected as active space of CASSCF. The energy gap between LS and HS states in π-hole-doped case (0.0007 a.u.) is smaller than that in σ-hole-doped case (0.0158 a.u). Though LS I and LS II states are not divided in CASSCF calculations of **1**, σ-hole-doped LS state is more stable than σ-hole-doped HS state and π-hole-doped HS state is more stable than π-hole-doped LS state. The energy gap between LS and HS states in π-hole is smaller than in σ-hole because of SE interaction. This supports the results of hybrid-DFT calculations.

DISCUSSION

The energy diagram of hole-doped states is explained by using d-p interaction between $3d_{x^2-y^2}$ orbital of copper and 2p orbital of oxygen and SE interaction between coppers via oxygen, as shown in Figure 4.



(4A)d-p interaction (4B)SE interaction

FIGURE 4 d-p interaction and SE interaction

In σ-hole of **1**, anti-parallel spin alignment is the most stable because of overlap between $3d_{x^2-y^2}$ orbital of copper and $2p_\sigma$ orbital of oxygen. The LS II state is the most stable, as all spin alignments between copper and oxygen are anti-parallel. As spin alignment between central oxygen and copper is parallel to one side and anti-parallel to other side in LS I state, LS I state is less stable than LS II state. The HS state among three spin states is the most unstable, as all spin alignments between copper and oxygen are parallel. In π-hole of **1**, parallel spin alignment between $3d_{x^2-y^2}$ orbital of copper and $2p_\pi$ orbital of oxygen is the most stable because of orthogonality between both orbitals. HS state is the most stable, as all spin alignments between copper and oxygen are parallel. As spin alignment between central oxygen and copper is parallel to one side and anti-parallel to other side, LS I state is less stable than HS state. The LS II state among three spin states is the most unstable, as all spin alignments between copper and oxygen are anti-parallel. In addition to this, LS state is more stabilized because of SE interaction between $3d_{x^2-y^2}$ orbital of copper via closed $2p_\sigma$ orbital of oxygen. LS state is close to HS state in Figure 2A.

For **2**, σ-hole-doped LS state is more stable than σ-hole-doped HS state, and π-hole-doped HS state is more stable than π-hole-doped LS state by d-p interaction as same as **1**. In addition to this, π-hole-doped LS state are extremely stabilized because of SE interaction between $3d_{x^2-y^2}$ orbital of copper via closed $2p_\sigma$ orbital of oxygen. π-hole-doped LS state is close to π-hole-doped HS state in Figure 2B. It is concluded that relative stability between LS and HS states in the hole-doped case is not changed by cluster models.

As long as comparing the relative stability of the σ- and π-hole-doped states for **1-3**, the π-hole-doped state is more stable, in accord with the GVB calculation[4]. This fact may suggest that larger clusters should be used when considering the hole-doped electronic states as the possible models of doped cuprates[5].

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References

[1.]J. G. Bednorz, K. A. Müller, *Z. Phys. B.* **64**, 189, (1986).
[2.]K. Yamaguchi et al, *Jpn. J. Appl. Phys.* **28**, 479 (1989)
[3.]J. E. Hirsch, S. Tang, *Sol. State. Comm.* **69**, 987 (1989)
[4.]Y. Guo, J-M. Langlois and A. Goddard III, *Science.* **239**, 896 (1988)
[5.]T. Tohyama and S. Maekawa, *Physica. C.* **191**, 193 (1992)
[6.]T. Onishi et al, *Polyhedron.* **20**. 1177 (2001).
[7.]T. Onishi et al, *Mol. Cryst. Liq. Cryst.* **343**, 133, (2000)