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Theoretical Studies on SDW and CDW States of Cu and Ag Oxides under the Periodic Boundary Condition

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SDW and CDW states of [-O-M-O-M-O-M-O-M-] (M=Cu, Ag) 4 site periodic model were investigated. Our theoretical attempt is to elucidate the difference among group 11 metals; Cu, Ag, from the view point of stability on SDW / CDW states, and leads to prospect of their physical properties.

Keywords SDW; CDW; charge fluctuation; periodic model; Cu and Ag oxides

INTRODUCTION

Doped cuprates are well known as high-Tc superconductors in two dimensional sheets. This mechanism is considered to originate from an antiferromagnetic spin fluctuation. However, existence of CDW or Charge Ordered States were also suggested in the cuprate, $PrBa_2Cu_4O_8$ [1,2]. While, Ag oxide

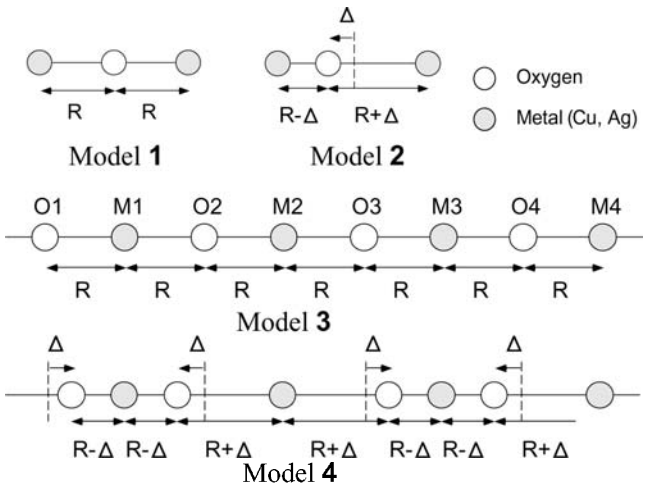

FIGURE 1 Structures of model **1** ~ **4**

and Au oxide have not been reported as high-Tc superconductors, though they belong to the same group 11 metal.

In the previous study [3], we focused on the stability of SDW / CDW states on metal oxides, which were investigated by using [M-O-M] (M = Cu, Ag, Au) minimum model. Among these metal oxides, we found the peculiar nature of Ag oxide that tends to become CDW state easily in comparison with Cu oxide. These calculations were, however, performed for the size-limited model, [M-O-M].

In this study, we examined the SDW / CDW stabilities of those metal-oxygen systems under the periodic boundary condition. They were investigated by changing metal-oxygen distance ($R_{M\text{-}O}$), and bond-alternation parameter (Δ) as illustrated in Figure 1.

COMPUTATIONAL DETAIL

In this study, we carried out *ab initio* Crystal Orbital calculations based on spin-polarized hybrid DFT (UB2LYP) and unrestricted HF method for

[-O-M-] periodic model. We considered 4 sites of [-O-M-], *i.e.* [-O-M-O-M-O-M-O-M-]$_n$, model as an unit cell (**3** and **4** in Figure 1) in order to discuss SDW, CDW, and other states. These calculations for model **3** and **4** were performed by using the CRYSTAL98 program package. As for basis functions, we employed 86-411-41dG for Cu, 8-411dG for O, and Hay and Wadt small core pseudopotential for Ag. The DFT code in the CRYSTAL98 needs the auxiliary basis set for the fitting of exchange and correlation potentials as well as electron density. We applied predefined even-tempered basis set of 12 s-type GTF. On the other hand, for size-limited model **1** and **2**, LANL2DZ for metals, and LANL2DZ which added diffuse and three polarization functions for O were used. These calculations for model **1** and **2** were performed by using the GAUSSIAN98 program package.

RESULTS AND DISCUSSION

Effect of Periodic Boundary Condition

Table 1 shows charge and spin density of various models of Cu oxide. Even though large basis functions (diffuse and three d-type polarization functions) were used for oxygen in size-limited models, 'edge' effect could not be negligible especially in case that terminal atoms were oxygen an-

TABLE 1 Charge (spin) density of Cu oxide for the low-spin SDW state of three clusters and one periodic model calculated by UB2LYP

Model	charge (spin)							
	O1	Cu1	O2	Cu2	O3	Cu3	O4	Cu4
Cu-O-Cu				1.62	-1.23	1.62		
				(0.96)	(0.00)	(-0.96)		
O-Cu-O-Cu-O			-1.50	1.43	-1.87	1.43	-1.50	
			(-0.78)	(1.62)	(0.00)	(-1.62)	(0.78)	
Cu-O-Cu-O-Cu-O-Cu		1.49	-1.45	1.87	-1.82	1.87	-1.45	1.49
		(0.97)	(0.03)	(-1.00)	(0.00)	(1.00)	(-0.03)	(-0.97)
[-O-Cu-O-Cu-O-Cu-O-Cu-]	-1.87	1.87	-1.87	1.87	-1.87	1.87	-1.87	1.87
	(0.00)	(0.95)	(0.00)	(-0.95)	(0.00)	(0.95)	(0.00)	(-0.95)

ion. Similarly the same tendency was obtained by the results of Cu oxide calculated by UHF, and Ag oxide done by UHF and UB2LYP. We concluded that charge and spin density, especially charge, obviously depended on model size.

Relative Stability in SDW / CDW Structure

(A) Difference of Cu oxide and Ag oxide in SDW

In Group 11 metal oxide, SDW state indicates [-O(-II)-M(II)-O(-II)-M(II)-] charge distribution. According to the results of calculations of model **3**, we found that Cu oxide easily took this charge state, while Ag oxide was unstable under such charge state. In case of Ag oxide, Ag tend to become Ag(I) closed shell instead of Ag(II) open shell. Figure 2 shows the relative energy of [-O(I)-Cu(I)-O(I)-Cu(I)-], [-O(II)-Cu(II)-O(II)-Cu(II)-], and [-O(I)-Ag(I)-O(I)-Ag(I)-], [-O(II)-Ag(II)-O(II)-Ag(II)-] in low and high spin states calculated by UHF. These relative energies were calculated by the difference from minimum energy of system and then divided by the

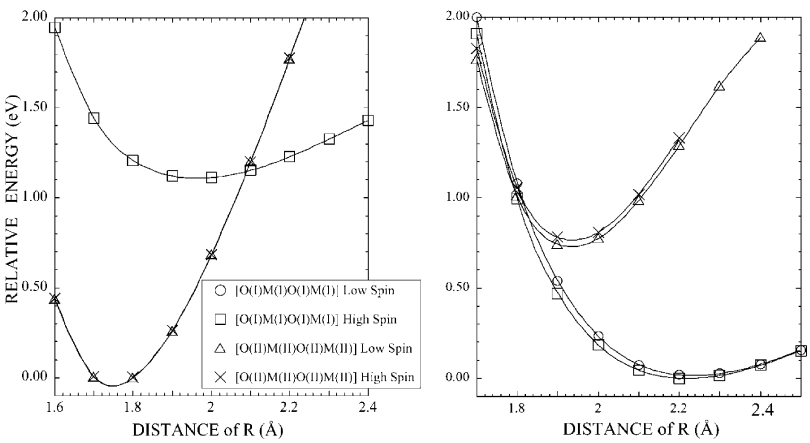

FIGURE 2 The relative energies of Cu (a) and Ag (b) oxides on the periodic model (see text).

number of bond (O-M). Ag^{2+} tended to be stable by taking electron from p-σ of O^{2-}, and then became [-O(I)-Ag(I)-O(I)-Ag(I)-] in most of all region. This tendency became obviously in the result of calculation by UB2LYP as shown in Figure 2b.

(B) Stability of CDW

In the previous study [3], Cu oxide and Ag oxide were calculated by using model **2**. From those results, we concluded that large R (2.3Å~) is necessary to stabilize the CDW in case of size-limited model. This tendency was also obtained from the periodic model **4**. Figure 3 shows that relative energy difference per bond calculated by UB2LYP. In Fig.3, an arrow points the meta-stable point ($R_{Ag1\text{-}O2}$=2.35, $R_{O2\text{-}Ag2}$=3.05) in CDW structure. Table 2 summarizes charge and spin of several stable points of SDW and CDW of Ag oxide. Charge fluctuation was obtained in size-limited model **2**. On the other hand, under the periodic boundary condition, such charge fluctuation could not be obtained as obvious as **2**. However, from Figure 3, we found that Ag oxide would easily be able to exhibit lattice distortion from. According to the Figure 3, relative energy was hardly affected by distortion in large R region (2.6Å~).

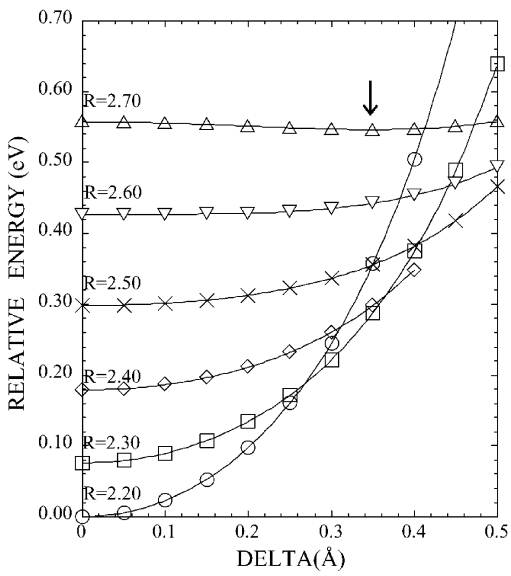

FIGURE 3 The relative energies of Ag oxide on the periodic model **4**

TABLE 2 Charge and spin density of size-limitted model **1, 2** and periodic model **3**, **4** of Ag oxide

Model				charge (spin)					R	Delta
	O1	Ag1	O2	Ag2	O3	Ag3	O4	Ag4		
1		1.18	-0.37	1.18					2.06	0.00
		(0.01)	(0.00)	(-0.01)						
2		1.28	-0.37	1.09					2.30	0.35
		(0.00)	(0.00)	(0.00)						
3	-0.82	0.82	-0.82	0.82	-0.82	0.82	-0.82	0.82	2.10	0.00
	(0.78)	(0.00)	(-0.78)	(0.00)	(0.78)	(0.00)	(-0.78)	(0.00)		
4	-0.85	0.80	-0.85	0.90	-0.85	0.80	-0.85	0.90	2.70	0.35
	(0.91)	(0.00)	(-0.91)	(0.00)	(0.91)	(0.00)	(-0.91)	(0.00)		

SUMMARY

In this study, we discussed (1) the effect of periodic boundary condition, (2) the relative stability of SDW / CDW state of Cu oxide and Ag oxide by using one dimensional periodic models. We concluded that periodic boundary condition was necessary for investigation of charge and spin density. Considering periodic boundary condition, CDW of Cu oxide and Ag oxide of one dimensional chain hardly became stable. However, we found that Ag(I) oxide shows the flexibility toward the lattice distortion. Extension of this lattice distortion to double chain is necessary as a next step.

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