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# Estimation of Transfer Matrix of AgO System

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The transfer matrices of $AgO_2$ plane and $Ag_2O_6$ chain are estimated by using the restricted open-shell B3LYP method. For $AgO_2$ plane, the charge transfer energy $\Delta$ between two sites is compared with that of $CuO_2$ plane. For $Ag_2O_6$ chain, the band structures are estimated by changing value of $\Delta$, and the conductivity of this chain is discussed in relation to the superconductivity from the analysis of band structures.

Keywords: silver oxide; transfer energy; superconductivity

## INTRODUCTION

Metal oxides have been attracted due to the interesting properties of magnetism and superconductivity and so on. Especially, copper oxide systems yield high-Tc superconductivity (HTCS) under the hole or electron doping. Since the discovery of HTCS by Bednorz and Müller in 1986[1], a lot of researches have been done experimentally and theoretically. Recently we have theoretically investigated the field-induced superconductivity of a model system of $CuO_2$ plane and molecular crystals of anthracene, oligothiophene and $C_{60}$ by using a two-band model based on the Green function techniques[2].

In this study, we estimate the transfer matrices of $AgO_2$ plane and

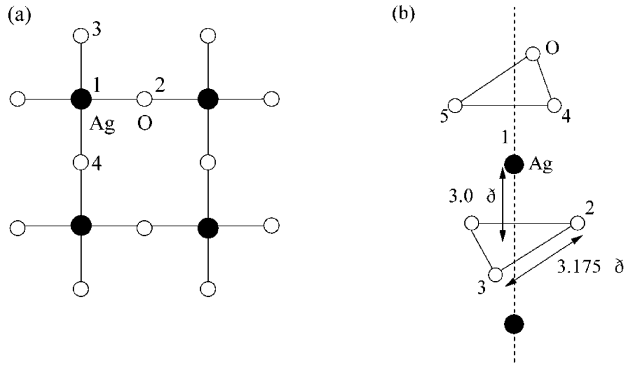


FIGURE 1 Model structures of AgO systems. (a) $AgO_2$ plane, (b) $Ag_2O_6$ chain. Arabic numbers refer to cite indices.

$Ag_2O_6$ chain by analyzing the molecular orbital energies obtained from the restricted open-shell Becke's gradient-corrected exchange correlation density functional (B3LYP) method[3]. To check the validity of this method applied in this study, we apply our method to $CuO_2$ plane, and compare our results with the other calculations. For the $AgO_2$ plane shown in Figure 1(a), we evaluate the transfer matrix $t_{ij}$ and charge transfer energy $\Delta$ of $AgO_2$ plane by changing Ag-O distance, and compare the results with those of $CuO_2$ plane. For the $Ag_2O_6$ chain shown in Figure 1(b), we estimate the band structures by changing the value of $\Delta$, and the conductivity of this chain is discussed in relation to the possibility of superconductivity from viewpoint of band structures.

## MODEL HAMILTONIAN

We used the following tight-binding Hamiltonian,

$$H = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{ij} t_{ij} c_i^\dagger c_j \tag{1}$$

where, $i$ refers to site indices, $\varepsilon_i$ is orbital energy at site $i$, and $t_{ij}$ is transfer parameter between sites $i$ and $j$. $c_i$ refers to the annihilation operator. Here we neglected the Coulomb repulsion.

## BASIS SET

All calculations in this study used effective core potential (ecp) and (3s3p2d) basis set for Ag and Cu. This basis set includes 4s (3s) and 4p (3p) orbitals for Ag (Cu) in the valence space. For O, (3s2p1d) basis set was used. All calculations was performed by GAUSSIAN98 program package[4].

## RESULTS AND DISCUSSION

### A. $AgO_2$ Plane

Transfer parameters $t_{23}$ and $t_{24}$ were estimated by two-atom model, where we take into account just for two relevant atoms. Then $t_{23}$ and $t_{24}$ were calculated from the energy difference between bonding and antibonding molecular orbital.

To calculate $t_{12}$ and charge transfer energy $\Delta$, we considered a unit cell consisting of Ag at site 1 and O at sites 2 and 3 in Figure 1(a). Then $t_{12}$ and $\Delta$ is given by

$$\Delta = \varepsilon_O - \varepsilon_{Ag} = 2E_0 - E_+ - E_- + 4t_{23} \tag{2}$$

$$t_{12}^2 = \{(E_+ - E_-)^2 - (\Delta + 2t_{23})^2\}/12 \tag{3}$$

where $E_0$, $E_+$ and $E_-$ are eigenvalues of the unit cell, and $\varepsilon_O$ ($\varepsilon_{Ag}$) represents the atomic energy of O (Ag).

At first, we considered $CuO_2$ plane that consists of $Cu^{2+}$ and $O^{2-}$ in order to check the validity of our method. Results are listed in Table 1, which shows that our method could yield the rather good value of transfer parameters qualitatively.

Table 1 Transfer parameters and charge transfer energy of $CuO_2$ plane in eV. Cu-O distance is 1.95 Å for present work.

| | Present | Ref. [5] | Ref. [6] | Ref. [7] |
|---|---|---|---|---|
| $\Delta$ | 2.3 | 2.3 | 2.3 | 2.2 |
| $t_{12}$ | 1.6 | 1.3 | 1.5 | 1.3 |
| $t_{23}$ | 0.64 | 0.65 | 0.60 | 0.65 |
| $t_{34}$ | 0.2 | - | - | - |

Next, we turn to $AgO_2$ plane. We here considered $Ag^{2+}$ and $Ag^{+}$. Figure 2 shows the change of $t_{ij}$ and $\Delta$ with respect to Ag-O distance, and we found that $t_{23}$ and $t_{34}$ for both $Ag^{2+}$ and $Ag^{+}$ decrease monotonically as Ag-O distance increases. However, $t_{12}$ and $\Delta$ shows the different behavior for $Ag^{2+}$ and $Ag^{+}$. $t_{12}$ for $Ag^{2+}$ has maximum at 1.8 Å, while $t_{12}$ of $Ag^{+}$ decreases monotonically. $\Delta$ for $Ag^{2+}$ was decreased monotonically, while for $Ag^{+}$ it has minimum at 2.0 Å. The behavior of $t_{12}$ and $\Delta$ for $Ag^{2+}$ are the same as $Cu^{2+}$ shown in figure 3.

From these results, we conclude that the behavior of $t_{12}$ and $\Delta$ may be strongly related to the ionic valency of a metal, and the changes of the conductivity of $CuO_2$ plane and $AgO_2$ plane with respect to metal-oxygen distance may show the different behavior because Ag atom tends to become easily $Ag^{+}$ rather than $Ag^{2+}$.

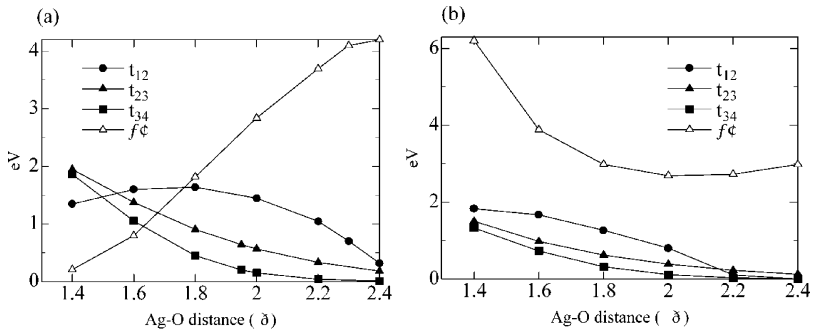


FIGURE 2 $t_{ij}$ and $\Delta$ of $AgO_2$ plane. (a) $Ag(II)O_2$, (b) $Ag(I)O_2$

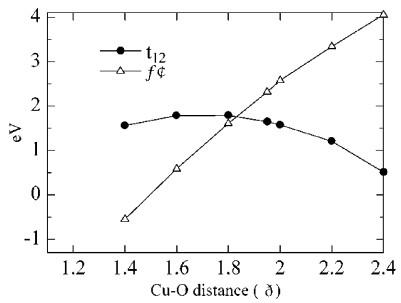


FIGURE 3 $t_{12}$ and $\Delta$ of $CuO_2$ plane.

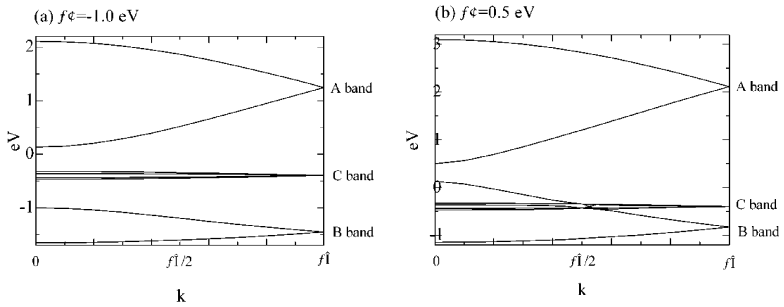


FIGURE 4 The band structure of $Ag_2O_6$ chain. k represents the wave number directed to the $Ag_2O_6$ chain. (a) $\Delta$ =-1.0 eV, $t_{12}$=0.41 eV. (b) $\Delta$ =0.5 eV, $t_{12}$=0.60 eV.

## B. $Ag_2O_6$ CHAIN

The structure of $Ag_2O_6$ chain is shown in Figure 1(b). We assumed the electric charges of Ag and O are 2+ and 2- respectively. In the present calculation, we estimated $t_{23}$ =0.40 eV, $t_{24}$ = 0.08 eV and $t_{25}$ = 0.13 eV by two-atom model. On the other hand, $t_{12}$ was calculated from

$$\Delta E = \sqrt{\Delta^2 + 4t_{12}^2}, \qquad \Delta = \varepsilon_{\mathrm{Ag}} - \varepsilon_{\mathrm{O}} \tag{4}$$

where, $\Delta E$ = 1.29 eV was estimated from the HOMO-LUMO gap energy of AgO molecule that consists of Ag at site 1 and O at site 2 in Figure 1(b). Here we changed $\Delta$ from -1.0 to 1.0 eV with the increment of 0.1 eV, and for each value of $\Delta$, we estimated the band structure of $Ag_2O_6$ chain. The band structure of $Ag_2O_6$ chain was consisted of two upper bands (A band), two lower bands (B band) and four nearly degenerated bands (C band). Band structures at $\Delta$=-1.0 and 0.5 eV are shown in Figure 4.

Conductivity does not appear at all value of $\Delta$, although C band crosses to B band for $\Delta$ = -0.4 ~ 0.9 eV. However, in this region, there is possibility of superconductivity phase by applying the field-effect transistor structure. Therefore, high- (room-) temperature superconductivity induced by external field might be appeared in this region according to the previous paper[2].

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