The Electronic Structure and Chemical Bonding between Metal and Oxygen Atoms: Tl22-Based Copper Oxide Superconductors

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Using tight-binding molecular orbital methods for charged cluster models, we studied the electronic structure and chemical bonding of thallium-oxygen and copper-oxygen atoms in Tl22-based copper oxide. The interaction between the s orbital of Tl atom and the p$_x$ and p$_y$ orbitals of O$_{3w}$ atoms in the Tl layers results in nonbonding. The interaction between the s orbital of Tl atom and the p$_x$ orbital of O$_2$ and O$_{3w}$ atoms in Ba and Tl layers results in antibonding. The interaction between the d$_{xy}$ orbital of Cu atom and the p$_x$ orbital of O$_2$ atom also results in antibonding. The Tl22-based copper oxide superconductors can be understood in terms of a local electron transfers from Cu layers to Tl layers along c-direction. The resulting electron transfers have the same patterns as those of YBa$_2$Cu$_3$O$_y$ and YBa$_2$Cu$_4$O$_8$ superconductors.

Introduction

At present Tl-based copper oxide superconductors show the highest superconducting transition temperatures $T_c$. The Tl-based copper oxide superconductors have Cu perovskite-like unit structures. These compounds can be divided into two types according to the space group. Type I that is Tl22-based copper oxide superconductors has space group P4/mmm. Type II that is Tl22-based copper oxide superconductors has the space group I4/mmm. The ideal superconducting phases of Tl22-based and Tl22-based copper oxide superconductors may be classified into six groups, TlBa$_2$CaCu$_2$O$_{6+}$Tl(Tl212 system)$^6$, TlBa$_2$Ca$_2$Cu$_3$O$_{6+}$Tl(Tl2212)$^7$, TlBa$_2$Ca$_3$Cu$_4$O$_{6+}$Tl(Tl234)$^8$, TlBa$_2$Cu$_2$O$_{6+}$Tl(Tl201)$^9$, TlBa$_2$CaCu$_2$O$_{6+}$Tl(Tl2223)$^9$, and TlBa$_2$Ca$_3$Cu$_4$O$_{6+}$Tl(Tl2223)$^9$.

The structures of these systems are separated by Tl-O monolayer and Ti-O bilayers for Tl22-based and Tl22-based copper oxide superconductors. Figure 1 shows nominal unit cells$^9$ for Tl2201, Tl2212, and Tl2223 superconductors. Ca$^{2+}$ cations are between adjacent Cu layers and Ba$^{2+}$ cations between Cu layers and Tl layers. From the comparison of the crystal structures of YBa$_2$Cu$_3$O$_y$ and Tl22-based copper oxide superconductors, copper-oxygen chains are present in a YBa$_2$Cu$_3$O$_y$ superconductor, while these chains are absent in Tl22-based copper oxide superconductors.

Using ASED-MO$^{10}$ of the tight-binding molecular orbital method, we studied electronic structures and chemical bonding of the thallium-oxygen and copper-oxygen atoms for Tl 22-based copper oxide superconductors.

The Cluster Size and Calculation Methods

The oxygen atoms in different layers of superconductors are crystallographically inequivalent. Tl22-based copper oxide superconductors are labeled by O1 (in Cu layers), O2 (in Ba layers), and O3 (in Tl layers). The atoms in the two inequivalent Cu layers are labeled Cu, Cu', and O1'. These labels are shown in Figure 1. We also use atoms O$_{3w}$ and O$_{3w}$, which stand for equatorial and axial positions in the Tl double layer for Tl22-based copper oxide superconductors.

Freeman et al.$^{11}$ and Kasowski et al.$^{12}$ calculated the band structure and electronic structure using the band theory for Tl22-based copper oxide superconductors. Their findings indicate that the Tl and Cu layers affect Fermi energy states. Using the full-potential linearized augmented plane-wave
method. Markstener et al.\textsuperscript{12} showed that Ca and Ba atoms in Tl22-based copper oxide superconductors are highly ionic and contributed little to the valence band density of state. In our calculations, we have selected the Tl and Cu atoms, though Ca and Ba atoms were used for Tl22-based copper oxide superconductors. Therefore, we have chosen O$_{3w}$-Tl-O$2$-Cu-O$2$, O$_{3w}$-Tl-O$2$-Cu-O$2$, O$_{3w}$-Tl-O$2$-Cu-Cu-O$2$ sequences along the c-direction including the Tl and Cu layers for Tl2201, Tl2212, and Tl2223 superconductors. The results of charged clusters are TiCu$_4$O$_8$H$_{14}^*$, TiCu$_4$O$_8$H$_{16}^-$, and TiCu$_4$O$_8$H$_{16}^-$ models for Tl2201, Tl2212, and Tl2223 superconductors. These models of charged clusters are shown in Figure 2. We also used point charge techniques with H atoms for the purpose of representing infinite solid to finite cluster. Atomic coordinates were taken from the X-ray crystallographic study of Tl2201, Tl2212, and Tl2223 superconductors by Torardi et al.\textsuperscript{15} and Subramanian et al.\textsuperscript{14}. Nominal valences per each atom are +3, +2, +2, -1, and +1 for Tl, Cu, O, and H, respectively. The parameters in tight-binding calculation, valence state ionization energy $H_0$, (eV) and exponent $\xi$, are shown in Table 1.

### Results and Discussion

#### Table 2. Interatomic Distances (r/Å), bond strength (s), and atomic valences (v) for Tl2201, Tl2212, and Tl2223 Superconductors

<table>
<thead>
<tr>
<th>System</th>
<th>Cu-O</th>
<th>r</th>
<th>s</th>
<th>v</th>
<th>number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl2201</td>
<td>Cu-O(1)</td>
<td>1.933</td>
<td>0.503</td>
<td>x 4</td>
<td></td>
</tr>
<tr>
<td>-O(2)</td>
<td>2.714</td>
<td>0.061</td>
<td>x 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.012(4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.134(6)</td>
<td></td>
</tr>
<tr>
<td>Tl2212</td>
<td>Cu(1)-O(1)</td>
<td>1.928</td>
<td>0.511</td>
<td>x 4</td>
<td></td>
</tr>
<tr>
<td>-O(2)</td>
<td>2.699</td>
<td>0.063</td>
<td>x 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.04(4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.10(5)</td>
<td></td>
</tr>
<tr>
<td>Tl2223</td>
<td>Cu(1)-O(1)</td>
<td>1.925</td>
<td>0.514</td>
<td>x 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu(2)-O(2)</td>
<td>1.927</td>
<td>0.512</td>
<td>x 4</td>
<td></td>
</tr>
<tr>
<td>-O(3)</td>
<td>2.480</td>
<td>0.115</td>
<td>x 1</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.04(4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.16(5)</td>
<td></td>
</tr>
</tbody>
</table>

*Reference 23. \textsuperscript{1}Reference 3. \textsuperscript{1}Reference 4. \textsuperscript{1}Reference 5. In this paper, the parentheses in atomic valences are coordination number of Cu atom. Numbers in sixth column are the number of equivalent O atoms surrounding Cu atom.

One of the common structural features for copper oxide superconductors is the existence of a Cu atom in a mixed-valence (2+ to 3+). The Ti atom\textsuperscript{19} for Tl22-based copper oxide superconductors exists in the mixed-valence. The mixed-valence of Ti atom (1+ to 3+) is made from Ti-6s band and conduction band of the Cu layers, as indicated by photoelectron spectroscopy\textsuperscript{19,20} and band calculations.\textsuperscript{21,22} We calculated the valence and strength of Cu atoms with four-, five-, and six-coordination numbers from the X-ray crystallographic data for Tl22-based copper oxide superconductors by Torardi et al.\textsuperscript{15} and Subramanian et al.\textsuperscript{14}. The effective mean valence of Cu atom is estimated from the relations of the bond length and bond strength.\textsuperscript{23} The calculated bond strengths and valences of Cu ion are listed in Table 2. The predicted valence values (and the coordination number) of the Cu ions is 2.012(4), 2.134(6), 2.04(4), 2.10(5), and 2.058(4) in the Cu$^1$ atom, 2.046(4), and 2.163(5) in the Cu$^1$ atom for Tl2201, Tl2212, and Tl2223 superconductors. The Cu atoms in the Cu layers have partial oxidation. Therefore, the Ti atoms in the Ti layers are partially reduced due to the polyhedra coordination of Cu atoms and orbital interactions of the O$_{3w}$-Tl-O$2$-Cu atoms along the c-direction. We find that the valence state of Ti atoms in the Ti layers and of Cu atoms in the Cu layers is <3+ and >2+. The electron distributions of the Ti and Cu layers with the coordination number of four and O$_{3w}$-Tl-O$2$ atoms along the c-direction are shown in Figures 3, 4, and 5. The electron distributions of the Ti and Cu layers with the coordination number of four are very similar to those with the coordination number for five or six for Tl2201, Tl2212, and Tl2223 superconductors. We have not presented the density of states (DOS) of the Ti and Cu layers with the coordination number of five and six. In DOS plots, the highest occupied energy
Figure 3. Total density of states (TDOS) and local density of states (LDOS) in TiCuO₃H₂⁺⁺ cluster model for Tl2201 superconductor. (a) TDOS in TiCuO₃H₂⁺⁺ cluster model. (b) LDOS in the Ti layer with the coordination number of four. (c) LDOS in the Cu layer with the coordination number of four. (d) LDOS in O₃₆–Tl–O₂ atoms along the c-direction.

Figure 4. Total density of states (TDOS) and local density of states (LDOS) in TiCuO₃H₂⁺⁺ cluster model for Tl2212 superconductor. (a) TDOS in TiCuO₃H₂⁺⁺ cluster model. (b) LDOS in the Ti layer with the coordination number of four. (c) LDOS in the Cu layer with the coordination number of four. (d) LDOS in O₃₆–Tl–O₂ atoms along the c-direction.

Figure 5. Total density of states (TDOS) and local density of states (LDOS) in TiCuO₃H₂⁺⁺ cluster model for Tl2223 superconductor. (a) TDOS in TiCuO₃H₂⁺⁺ cluster model. (b) LDOS in the Ti layer with the coordination number of four. (c) LDOS in the Cu layer with the coordination number of four. (d) LDOS in the Cu layer with the coordination number of four. (e) LDOS in O₃₆–Tl–O₂ atoms along the c-direction.

Table 3. Orbital Overlap Populations of Tl, Cu, and O Atoms in the Ti, Cu, and Ba Layers for Tl2201, Tl2212, and Tl2223 Superconductors

<table>
<thead>
<tr>
<th>Orbital-Orbital</th>
<th>Tl2201</th>
<th>Tl2212</th>
<th>Tl2223</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl 6s–O₃₆, pₓ</td>
<td>–0.078</td>
<td>–0.058</td>
<td>–0.050</td>
</tr>
<tr>
<td>Tl 6s–O₂, pₓ</td>
<td>–0.038</td>
<td>–0.017</td>
<td>–0.064</td>
</tr>
<tr>
<td>O₂ pₓ–Cu dₓ²</td>
<td>–0.002</td>
<td>–0.002</td>
<td>–0.006</td>
</tr>
</tbody>
</table>

The overlap populations for Tl2201, Tl2212, and Tl2223 superconductors, the chemical bonds in pₓ orbital of the O₃₆ atom with s orbital of the Ti atom and the pₓ orbital of the O₂ atom with the s orbital of the Ti atom indicate antinote antibondings. Our calculations agree with those of Freeman et al. and Kasowski et al. using band calculations. The chemical bonds of the pₓ orbital of the O₂ atom with dₓ² orbital of the Cu atom are also antibonding for Tl2201, Tl2212, and Tl2223 superconductors. The calculated orbital overlap populations are shown in Table 3. In the Ti layers, the chemical bond of the s orbital of Ti atom with pₓ or pᵧ orbital of O₃₆, atom are weaker than that of the s orbital of Ti atom with the pₓ orbital of O₂ and O₃₆ atoms. It is because Tl–O₃₆ interatomic distances (2.496, 2.462, 2.49 Å for Tl2201, Tl2212, and Tl2223 superconductors) are larger than Ti₃⁺ and O²⁻ ionic radii (2.25 Å) and Ti–O₂ (1.995, 1.978, 2.20 Å for Tl2201, Tl2212, and Tl2223 superconductors).

We studied local charge transfers from the Cu layers to the Ti layers. From the decomposition of crystal orbital overlap populations for Tl2201, Tl2212, and Tl2223 superconductors, the chemical bonds in pₓ orbital of the O₃₆ atom with s orbital of the Ti atom and the pₓ orbital of the O₂ atom with the s orbital of the Ti atom indicate antinote antibondings. Our calculations agree with those of Freeman et al. and Kasowski et al. using band calculations. The chemical bonds of the pₓ orbital of the O₂ atom with dₓ² orbital of the Cu atom are also antibonding for Tl2201, Tl2212, and Tl2223 superconductors. The calculated orbital overlap populations are shown in Table 3. In the Ti layers, the chemical bond of the s orbital of Ti atom with pₓ or pᵧ orbital of O₃₆, atom are weaker than that of the s orbital of Ti atom with the pₓ orbital of O₂ and O₃₆ atoms. It is because Tl–O₃₆ interatomic distances (2.496, 2.462, 2.49 Å for Tl2201, Tl2212, and Tl2223 superconductors) are larger than Ti₃⁺ and O²⁻ ionic radii (2.25 Å) and Ti–O₂ (1.995, 1.978, 2.20 Å for Tl2201, Tl2212, and Tl2223 superconductors).

We studied local charge transfers from the Cu layers to the Ti layers. From the decomposition of crystal orbital overlap populations for Tl2201, Tl2212, and Tl2223 superconductors, we compared Ti layers, Cu layers, and O₃₆–Tl–O₂ atoms along the c-direction to see the result of the total density of states (TDOS) and the local density of states (LDOS). In nearby HOEL, the electron distributions are present in the Ti layers and O₂–Tl–O₃₆ atoms along the c-direction, while they are not present in the Cu layers. For Tl2223 superconductors, the electron distributions in the Cu layers are very similar to the Cu’ layers. The LDOS patterns in the Cu and Cu’ layers for Tl22-based copper oxide superconductors are from the structural characteristics. We know that the Cu layers act as electron donor states, while the Ti layers act as electron acceptor states.

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Figure 6. Schematic diagrams of the local charge transfer inferred from the tight-binding MO studies. (a) Y123 superconductor. (b) Tl223 superconductor.

Tl223 superconductors are shown in Figure 6. The structural differences between Y123 and Tl22-based copper oxide superconductors show the Cu-O chains are present in the Y123 and superconductor, while they are not present in the Tl22-based copper oxide superconductors. If the structures of Cu-O chains are distinguished from those of Y123 and Tl22-based copper oxide superconductors, the Tl layers for Tl22-based copper oxide superconductors are the same as the Cu-O chains for Y123 superconductor. Namely, the Cu-O chains and the Ti layers are in electron acceptor states.

References