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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 structrue 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 $O3_{eq}$ atom in the Tl layers results in nonbonding. The interaction between the s orbital of Tl atom and the p_z orbital of O2 and $O3_{ax}$ atoms in Ba and Tl layers results in antibonding. The interaction between the d_{z^2} orbital of Cu atom and the p_z orbital of O2 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 $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ superconductors.

Introduction

At present Tl-based copper oxide superconductors show the highest superconducting transition temperatures T_c[1-5]. 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 Tl12-based copper oxide superconductors has space group P4/mmm. Type II that is Tl22-based copper oxide supeconductors has the space group I4/mmm. The ideal superconducting phases of Tl12-based and Tl22-based copper oxide superconductors may be classified into six groups, $TlBa_2CaCu_2O_7$(Tl1212 system)[6], $TlBa_2Ca_2Cu_3O_{10}$(Tl1223)[7], $TlBa_2Ca_3Cu_4O_{11}$(Tl1234)[8], $Tl_2Ba_2CuO_6$(Tl2201)[3], $Tl_2Ba_2CaCu_2O_8$(Tl2212)[4], and $Tl_2Ba_2Ca_2Cu_3O_{10}$(Tl2223)[5].

The structures of these systems are separated by Tl-O monolayer and Tl-O bilayers for Tl12-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 $YBa_2Cu_3O_7$ and Tl22-based copper oxide superconductors, copper-oxygen chains are present in a $YBa_2Cu_3O_7$ 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 ineqivalent. 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, O1, Cu′ and O1′. These labels are shown in Figure 1. We also use atoms $O3_{eq}$ and $O3_{ax}$ which stand for equatorial and axial positions in the Tl double layer for Tl22-based copper oxide superconductors.

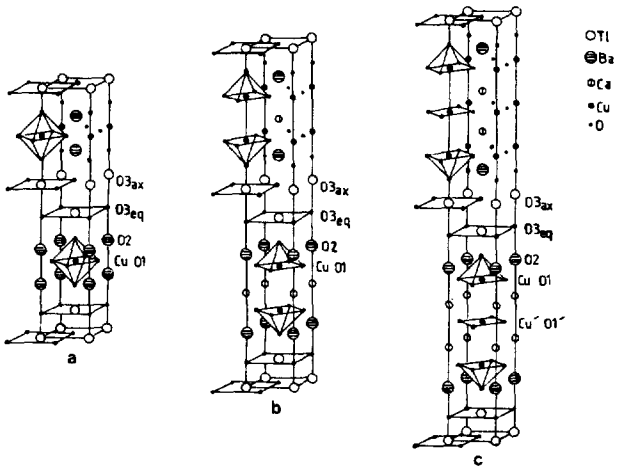

Figure 1. Nominal unit cells for $Tl_2Ba_2CuO_6$, $Tl_2Ba_2CaCu_2O_8$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductors. (a) $Tl_2Ba_2CuO_2$ superconductors. (b) $Tl_2Ba_2CaCu_2O_8$ superconductor. (c) $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductors.

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

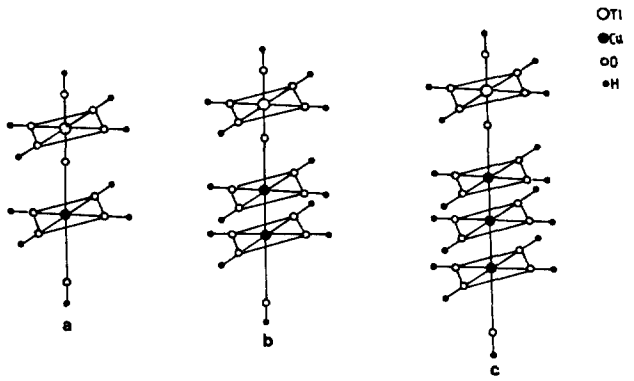

Figure 2. Models of clusters in calculation for $Tl_2Ba_2CuO_6$, $Tl_2Ba_2CaCu_2O_8$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductors. (a) $TlCuO_{11}H_{10}^{7-}$ cluster model for Tl2201 superconductor. (b) $TlCu_2O_{15}H_{14}^{9-}$ cluster model for Tl2212 superconductor. (c) $TlCu_3O_{19}H_{18}^{11-}$ cluster model for Tl2223 superconductor.

Table 1. Atomic Parameters Used in the Calculations

Atom	Orbital	H_{ij} (eV)	Exponents[e]	
			ζ_1	ζ_2
Tl[a]	6*s*	−16.20	2.370	
	6*p*	−9.00	1.970	
Cu[b]	4*s*	−11.40	2.200	
	4*p*	−6.06	2.200	
	3*d*	−14.00	5.950 (0.5933)	2.300 (0.5744)
O[c]	2*s*	−28.48	2.246	
	2*p*	−13.62	2.227	
H[d]	1*s*	−13.60	2.200	

[a]Reference 14. [b]Reference 15. [c]Reference 16. [d]Reference 17. [e]Each is followed in parentheses by the coefficients in the double zeta expansion.

method, Markstener *et al.*[13] 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 $O3_{ax}$-Tl-O2-Cu-O2, $O3_{ax}$-Tl-O2-Cu-Cu-O2, $O3_{ax}$-Tl-O2-Cu-Cu-Cu-O2 sequences along the *c*-direction including the Tl and Cu layers for Tl2201, Tl2212, and Tl2223 superconductors. The results of charged clusters are $TlCuO_{11}H_{10}^{7-}$, $TlCu_2O_{15}H_{14}^{9-}$, $TlCu_3O_{19}H_{18}^{11-}$ models for Tl2201, Tl2212, and Tl223 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.*[3,5] and Subramanian *et al.*[4]. Nominal valences per each atoms are 3+, 2+, 2− and 1+ for Tl, Cu, O, and H, respectively. The parameters in tight-binding calculation, valence state ionization energy H_{ij} (eV) and exponent ξ, are shown in Table 1.

Results and Discussion

Table 2. Interatomic Distances (r/Å), bond strength (s)[a], and atomic valences (v)[b] for Tl2201[c], Tl2212[d], and Tl2223[e] Superconductors

System	Cu-O	r	s	v	number[g]
Tl2201	Cu-O(1)	1.933	0.503		x 4
	-O(2)	2.714	0.061		x 2
				2.012(4)[f]	
				2.134(6)	
Tl2212	Cu(1)-O(1)	1.928	0.511		x 4
	-O(2)	2.699	0.063		x 1
				2.044(4)	
				2.107(5)	
Tl2223	Cu(1)-O(1)	1.925	0.514		x 4
				2.056(4)	
	Cu(2)-O(2)	1.927	0.512		x 4
	-O(3)	2.480	0.115		x 1
				2.048(4)	
				2.163(5)	

[a,b]Reference 23. [c]Reference 3. [d]Reference 4. [e]Reference 5. [f]In this paper, the parentheses in atomic valences are coordination number of Cu atom. [g]Numbers in sixth column are the number of equivalent O atoms surrounding Cu atom.

One of the common structural features[4] for copper oxide superconductors is the existence of a Cu atom in a mixed-valence (2+ to 3+). The Tl atom[18] for Tl22-based copper oxide superconductors exists in the mixed-valence. The mixed-valence of Tl atom (1+ to 3+) is made from Tl-6*s* band and conduction band of the Cu layers, as indicated by photoelectron spectroscopy[19,20] and band calculations[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.*[3,5] and Subramanian *et al.*[4]. The effective mean valence[23] of Cu atom is estimated from the relations of the bond length and bond strength[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), 2.044(4), 2.107(5), 2.058(4) in the Cu1′ atom, 2.048(4), and 2.163(5) in the Cu1 atom for Tl2201, Tl2212, and Tl2223 superconductors. The Cu atoms in the Cu layers have partial oxidation. Therefore, the Tl atoms in the Tl layers are partially reduced due to the polyhedra coordination of Cu atoms and orbital interactions of the $O3_{ax}$-Tl-O2-Cu atoms along the *c*-direction. We find that the valence state of Tl atoms in the Tl layers and of Cu atoms in the Cu layers is $<3+$ and $>2+$.

The electron distributions of the Tl and Cu layers with the coordination number of four and $O3_{ax}$-Tl-O2 atoms along the *c*-direction are shown in Figures 3, 4, and 5. The electron distributions of the Tl 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 Tl and Cu layers with the coordination number of five and six. In DOS plots, the highest occupied energy

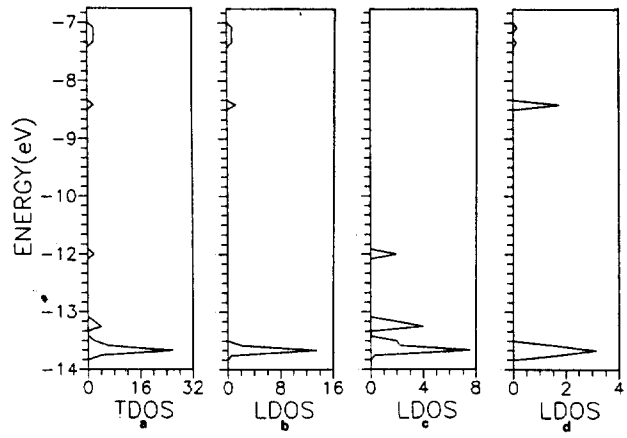

Figure 3. Total density of states (TDOS) and local density of states (LDOS) in $TlCuO_{11}H_{10}^{7-}$ cluster model for Tl2201 superconductor. (a) TDOS in $TlCuO_{11}H_{10}^{7-}$ cluster model. (b) LDOS in the Tl layer with the coordination number of four. (c) LDOS in the Cu layer with the coordination number of four. (d) LDOS in $O3_{ax}$-Tl-O2 atoms along the *c*-direction.

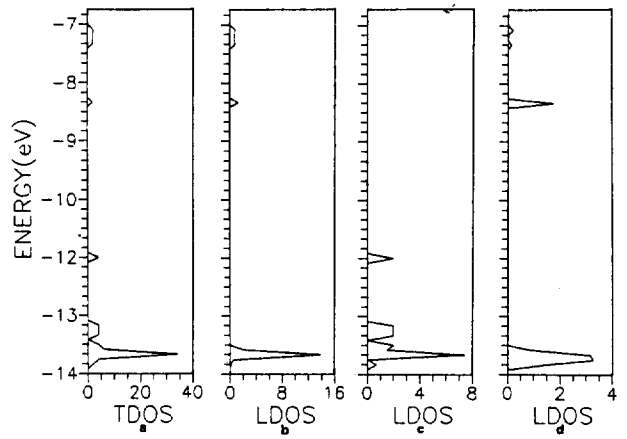

Figure 4. Total density of states (TDOS) and local density of states (LDOS) in $TlCu_2O_{15}H_{14}^{9-}$ cluster model for Tl2212 superconductor. (a) TDOS in $TlCu_2O_{15}H_{14}^{9-}$ cluster model. (b) LDOS in the Tl layer with the coordination number of four. (c) LDOS in the Cu layer with the coordination number of four. (d) LDOS in $O3_{ax}$-Tl-O2 atoms along the *c*-direction.

level (HOEL) is −6.9, −7.09, −7.06 eV for Tl2201, Tl2212, and Tl2223 superconductors. We compared Tl layers, Cu layers, and $O3_{ax}$-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 Tl layers and O2-Tl-$O3_{ax}$ 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 Tl layers act as electron acceptor states.

We studied local charge transfers from the Cu layers to the Tl layers. From the decomposition of crystal orbital over-

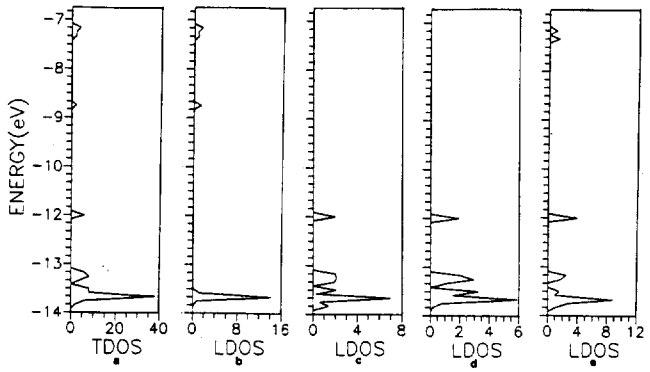

Figure 5. Total density of states (TDOS) and local density of states (LDOS) in $TlCu_3O_{19}H_{18}^{11-}$ cluster model for Tl2223 superconductor. (a) TDOS in $TlCu_3O_{19}H_{18}^{11-}$ cluster model. (b) LDOS in the Tl layer with the coordination number of four. (c) LDOS in the Cu′ layer with the coordination of four. (d) LDOS in the Cu layer with the coordination number of four. (e) LDOS in $O3_{ax}$-Tl-O2 atoms along the c-direction.

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

Orbital-Orbital	Tl2201	Tl2212	Tl2223
Tl 6*s*-$O3_{ax}$ p_z	−0.078	−0.058	−0.050
Tl 6*s*-O2 p_z	−0.038	−0.017	−0.064
O2 p_z-Cu d_z^2	−0.002	−0.002	−0.005

lap populations for Tl2201, Tl2212, and Tl2223 superconductors, the chemical bonds in p_z orbital of the $O3_{ax}$ atom with *s* orbital of the Tl atom and the p_z orbital of the O2 atom with the *s* orbital of the Tl atom indicate anticate antibondings. Our calculations agree with those of Freeman *et al.*[11] and Kasowski *et al.*[12] using band calculations. The chemical bonds of the p_z orbital of the O2 atom with d_z^2 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 Tl layers, the chemical bond of the *s* orbital of Tl atom with p_x or p_y orbital of $O3_{eq}$ atom are weaker than that of the *s* orbital of Tl atom with the p_z orbital of O2 and $O3_{ax}$ atoms. It is because Tl-$O3_{eq}$ interatomic distances (2.496, 2.462, 2.48 Å for Tl2201, Tl2212, and Tl2223 superconductors) are larger than Tl^{3+} and O^{2-} ionic radii (2.25 Å) and Tl-O2 (1.995, 1.978, 2.20 Å for Tl2201, Tl2212, and Tl2223 superconductors), $-O3_{ax}$ (2.038, 2.031, 1.92 Å for Tl2201, Tl2212, and Tl2223 superconductors) interatomic distances are smaller. In superconducting state for Tl22-based copper oxide superconductors, the electrons in the Cu layers can move the Tl layers along the *c*-direction. Our calculational results are similar to position distribution contributions by Bharathi *et al.*[24] who have shown electron transfer from the planar O atom to the apical O atom for Tl2223 superconductor. We have published local charge transfers for $YBa_2Cu_3O_7$(Y123) and $YBa_2Cu_4O_8$(Y124) superconductors[25-28]. We have found the local charge transfers of Y123 and Y124 superconductors move the Cu layers to the Cu chains. Our charge transfer models for Y123 and

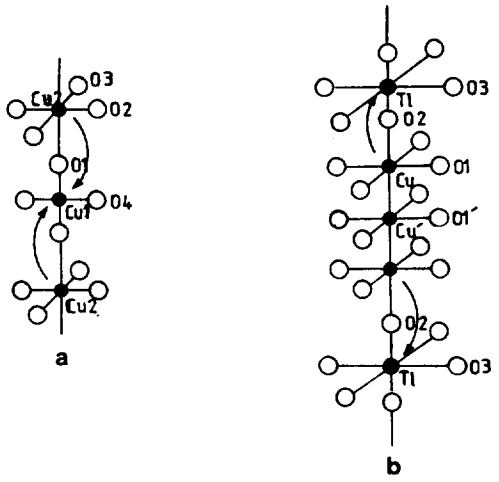

Figure 6. Schematic diagrams of the local charge transfer inferred from the tight-binding MO studies. (a) Y123 superconductor. (b) Tl2223 superconductor.

Tl2223 superconductors are show 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 Tl layers are in electron acceptor states.

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