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Electronic Structure Study of the Formal Oxidation States of Thallium, Lead, and Bismuth in the $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ Superconductors ($A = Tl_{0.5}Pb_{0.5}$, $Tl_{0.5}Bi_{0.5}$)

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We examined the formal oxidation states of Pb and Bi in the single rock salt layer superconductors $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ ($A = Tl_{0.5}Pb_{0.5}$, $Tl_{0.5}Bi_{0.5}$; $n = 2,3$) by performing tight-binding band electronic structure calculations on the distorted AO_3 layers and also molecular orbital calculations on the distorted AO_6 octahedra. Our results show that the most likely oxidation state of Pb is +4, and that of Bi is either +3 or +5. The similarities in the T_c values of $(Tl_{0.5}Pb_{0.5})Sr_2CaCu_2O_7$ and $(Tl_{0.5}Bi_{0.5})Sr_2CaCu_2O_7$ suggest that the Bi atoms of $(Tl_{0.5}Bi_{0.5})Ca_{n-1}Cu_nO_{2n+3}$ are half in the +3 and half in the +5 oxidation states. Thus the Pb and Bi atoms of $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ lower the copper oxidation state with respect to that of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$.

The members of the homologous copper oxide superconducting series $A_mB_2Ca_{n-1}Cu_nO_{2n+m+2}$ ($A = Tl$, Bi; $B = Ba$, Sr; $m = 1,2$; $n = 1$–3)[1] contain perovskite Cu–O layers and rock salt A–O layers as their structural building blocks. The m values are 1 and 2 when these compounds have single and double rock salt A–O layers, respectively. For B = Ba both single and double rock salt layer compounds are known when A = Tl, while for B = Sr only double rock salt layer compounds are found when A = Bi. Single rock salt layer compounds with B = Sr, i.e., $ASr_2Ca_{n-1}Cu_nO_{2n+3}$, are obtained if A is a mixture such as $Tl_{0.5}Pb_{0.5}$ or $Tl_{0.5}Bi_{0.5}$.[2,3] The superconducting transition temperatures T_c of these phases are relatively high: the T_c (zero resistivity) values of $(Tl_{0.5}Pb_{0.5})Sr_2CaCu_2O_7$, $(Tl_{0.5}Bi_{0.5})Sr_2CaCu_2O_7$, and $(Tl_{0.5}Pb_{0.5})Sr_2Ca_2Cu_3O_9$ are 82, 90, and 114 K, respectively.

A recent band electronic structure study[4] has shown that the Tl 6s-block bands of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ lie well above the Fermi level (i.e., the formal oxidation state of Tl is +3) and thus do not remove electrons from the CuO_2 layer $x^2 - y^2$ bands. Namely, the single rock salt Tl–O layers of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ do not act as a hole source.[4] This finding is consistent with the observation that the copper oxidation state of stoichiometric $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ is already so high (e.g., +3.00, +2.50, and +2.33 for $n = 1$–3, respectively, if the oxidation states of Tl^{3+}, Ba^{2+}, Ca^{2+}, and O^{2-} are assumed) that electron removal from the CuO_2 layers by the single rock salt Tl–O layers seems unnecessary. The single rock salt A–O layer of $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ ($A = Tl_{0.5}Pb_{0.5}$, $Tl_{0.5}Bi_{0.5}$) is similar in structure to the corresponding layer of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, so that the Tl oxidation state in $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ is expected to be +3. In understanding the superconductivity of the $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ series, it is crucial to know the formal oxidation states of their Pb and Bi atoms since they provide information concerning whether or not the role of the Pb and Bi atoms in $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ ($A = Tl_{0.5}Pb_{0.5}$, $Tl_{0.5}Bi_{0.5}$) is to reduce the copper oxidation state with respect to that in $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$. In the present work, we probe this question by carrying out tight-binding band electronic structure calculations[5] on several model rock salt A–O layers and also molecular orbital calculations on model AO_6 clusters of $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ within the framework of the extended Hückel method.[6] The atomic parameters employed in the present study are summarized in Table I.

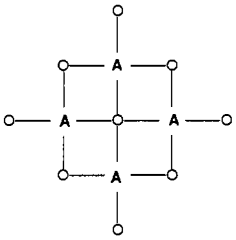
Table I. Atomic Parameters Used in the Calculations

atom	orbital	H_{ii}, eV	$\zeta_1{}^a$	$\zeta_2{}^a$	$c_1{}^b$	$c_2{}^b$
Tl	6s	−16.2	2.37			
	6p	−9.0	1.97			
Pb	6s	−18.7	2.57			
	6p	−10.8	2.13			
Bi	6s	−21.2	2.76			
	6p	−12.6	2.29			
Cu	4s	−11.4	2.20			
	4p	−6.06	2.20			
	3d	−14.0	5.95	2.30	0.5933	0.5744
O	2s	−32.3	2.275			
	2p	−14.8	2.275			

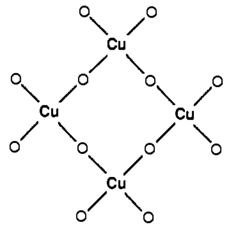
[a] Slater type orbital exponents. [b] Contraction coefficients of a double-ζ expansion.

Distortion of the Single Rock Salt AO_3 Layer

The AO_3 layer of $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ can be constructed in terms of AO_6 octahedra upon sharing the octahedral edges of their equatorial oxygen (O_{eq}) atoms. The single rock salt A–O_{eq} sheet of the AO_3 layer is shown in **1**. The axial oxygen atoms (O_{ax}) of the AO_3 layer are shared with the Cu atoms of the neighboring perovskite CuO_2 layers **2** to form linear A–O_{ax}–Cu linkages perpendicular to the CuO_2 sheet. When the A–O_{eq} sheet of an ideal AO_3 layer is represented by **3a**, the positions of A and O_{eq} in the distorted AO_3 layer (as found in $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ with $A = Tl_{0.5}Pb_{0.5}$ for $n = 2$ and 3) are each given by four split positions as shown in **3b** around the ideal positions of **3a**.[2] Previous band electronic structure calculations on $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$[7]



1



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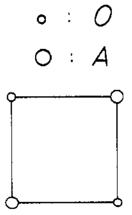
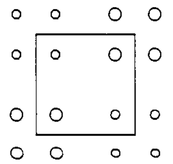


3a



3b

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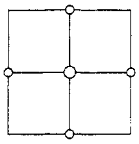
and $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$[4] showed that such rock salt layer distortions have profound effects on the positions of the rock salt layer bands (e.g., Bi 6p- and Tl 6s-block bands) with respect to the Fermi level and therefore on the hole concentration in the CuO_2 layers. Thus in electronic structure calculations on $ASr_2Ca_{n-1}Cu_nO_{2n+3}$, it is necessary to consider several model structures of the AO_3 layer that can be generated by choosing one of the four positions for A and O_{eq}. Since the nature and the extent of the AO_3 layer distortions in $(Tl_{0.5}Pb_{0.5})Sr_2CaCu_2O_7$ and $(Tl_{0.5}Pb_{0.5})Sr_2Ca_2Cu_3O_9$ are almost the same,[2] we construct several model structures of the AO_3 layer on the basis of the crystal structure of $(Tl_{0.5}Pb_{0.5})Sr_2Ca_2Cu_3O_7$.[2] The arrangement of four O_{eq} atoms around A in the ideal AO_3 layer is given by **4a** ($A–O_{eq}$ = 2.69 Å). The arrangements **4b,c** are two examples in which the $A–O_{eq}$ bonds are longer than those of **4a** ($A–O_{eq}$ = 2.97 Å in **4b**; $A–O_{eq}$ = 2.82 and 3.17 Å in **4c**). Likewise, **4d** and **4e** are two examples in which the $A–O_{eq}$ bonds are shorter compared with those of **4a** ($A–O_{eq}$ = 2.44 Å in **4d**; $A–O_{eq}$ = 2.25 and 2.61 Å in **4e**). Though not shown, there exist many other possible arrangements that lie between the above extremes.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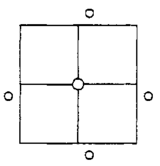
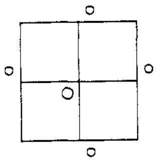

4b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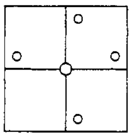
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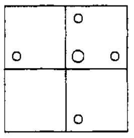
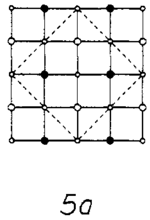

4e

In constructing the ideal and the distorted structures of the AO_3 layers of $ASr_2Ca_{n-1}Cu_nO_{2n+3}$, it is necessary to consider how to distribute two different cations in the AO_3 layers (e.g.: Tl and Pb; Tl and Bi). **5a–c** are three simple $A–O_{eq}$ sheet patterns examined in our study, where unit cells are shown by dashed lines. **5a,c** have four A sites per unit cell, and **5b** has two A sites per unit cell. In the ideal pattern **5a**, all A sites have equal $A–O_{eq}$ bonds. **5b** has two nonequivalent A sites, one with four short and the other with four long $A–O_{eq}$ bonds. **5c** has three nonequivalent A sites, one with four short, one with two short and two long, and one with four long $A–O_{eq}$ bonds. To simulate the distorted AO_3 layers with A = $Tl_{0.5}Pb_{0.5}$ or $Tl_{0.5}Bi_{0.5}$, we distribute the Tl and M (=Pb or Bi) atoms as shown in **5a–c**, where the large empty and filled circles represent Tl and M atoms respectively. Certainly, there are many other possible $A–O_{eq}$ sheet patterns and Tl/M atom distributions, but the three examples **5a–c** are sufficient for our purposes as will be discussed later.

◦ : O ○ : Tl ● : Pb or Bi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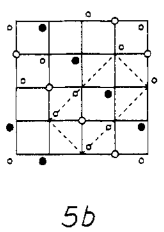
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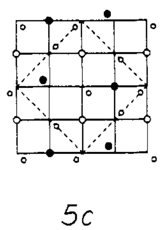
5c

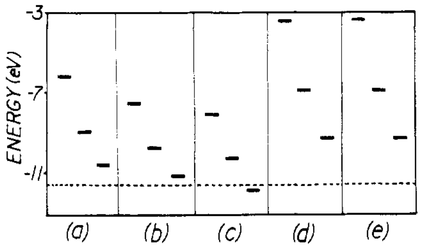

Figure 1. 6s-block levels calculated for the AO_6 octahedra (A = Tl, Pb, Bi) with the $A–O_{eq}$ arrangements of (a) **4a**, (b) **4b**, (c) **4c**, (d) **4d**, and (e) **4e**. In each column a–e, the top, the middle, and the bottom levels refer to the 6s-block levels of Tl, Pb, and Bi, respectively.

Electronic Structure

In copper oxide superconductors, the highest occupied bands (i.e., the $x^2 - y^2$ bands) of the CuO_2 perovskite layers are primarily constructed from the $x^2 - y^2$ orbitals of the copper atoms and the p orbitals of the in-plane oxygen atoms. The $x^2 - y^2$ orbital of copper is a δ orbital with respect to the $Cu–O_{ax}–A$ axis, so that the $x^2 - y^2$ orbital practically does not overlap with any orbital of O_{ax} and A. Consequently, the $x^2 - y^2$ bands of the CuO_2 layers do not have any orbital contribution from the A–O rock salt layers. Likewise, the s- and p-block bands of the A–O rock salt layers have no $x^2 - y^2$ orbital contribution from the CuO_2 perovskite layers. Therefore, the s- and p-block bands of the A–O rock salt layers are essentially the same regardless of whether they are calculated for the whole crystal lattice including the CuO_2 perovskite layers or for an isolated A–O rock salt layer. For simplicity of calculations, we adopt the latter approach in our study.

A. AO_6 Octahedra. We performed molecular orbital calculations on a number of AO_6 octahedra (A = Tl, Pb, Bi) to examine how their 6s-block levels are affected by the $A–O_{eq}$ sheet distortions in the AO_3 layer. The 6s-block levels of the AO_6 octahedra having the $A–O_{eq}$ bond arrangements **4a–e** are shown in Figure 1, where the Fermi level of the half-filled $x^2 - y^2$ bands of the CuO_2 layers (taken from $ASr_2Ca_2Cu_3O_9$[2]) is shown by the dashed line. The essential features of Figure 1 can be summarized as follows: (a) With respect to the ideal AO_6 octahedron **4a**, shortening and lengthening of the $A–O_{eq}$ bonds lead to higher and lower lying 6s-block levels, respectively, for all AO_6 (A = Tl, Pb, Bi). This reflects the fact that the 6s-block levels of AO_6 octahedra are antibonding in the A–O bonds. (b) The 6s-block levels of Tl and Pb are well above the Fermi level even when the surrounding $A–O_{eq}$ (A = Tl, Pb) bonds are long. Thus the most likely oxidation states of Tl and Pb are +3 and +4, respectively (i.e., their 6s-block levels are not occupied). (c) The 6s-block level of Bi lies below or close to the Fermi level for the AO_6 octahedra with long $A–O_{eq}$ bonds but well above the Fermi level for those with short $A–O_{eq}$ bonds. Thus the Bi oxidation state can be either +3 (i.e., the 6s-block band is filled) or +5 (i.e., the 6s-block band is empty) depending upon the coordinate environment of Bi.

B. AO_3 Layers. As described in the previous section, the 6s-block levels of the AO_6 (A = Tl, Pb, Bi) octahedra lie generally high in energy. Of the elements Tl, Pb, and Bi, the atom Bi is most electronegative and has the most contracted atomic orbitals. Given the same $A–O_{eq}$ bonds, the lowest lying 6s-block level of AO_6 occurs for A = Bi. Even for this case, the 6s-block level lies below the Fermi level only when the $Bi–O_{eq}$ bonds are long. Thus in our band electronic structure calculations on the AO_3 layers (A = $Tl_{0.5}Pb_{0.5}$, $Tl_{0.5}Bi_{0.5}$), it is important to examine whether or not the lowest lying possible 6s-block bands originating from M (=Pb, Bi) lie below the Fermi level. Consequently, we calculate the band electronic structures of the AO_3 layers having the $A–O_{eq}$ sheet patterns **5a–c**. In the ideal pattern **5a**, each M is surrounded by four Tl atoms, and each Tl by four M atoms. In the distorted pattern **5b**, all M and Tl atoms are located at the sites with four long and four short $A–O_{eq}$ bonds, respectively. In **5c** all Tl atoms are placed at the sites with two short and two long $A–O_{eq}$ bonds, while the M atoms are half at the sites with four long $A–O_{eq}$ bonds and half at those with four short $A–O_{eq}$ bonds.

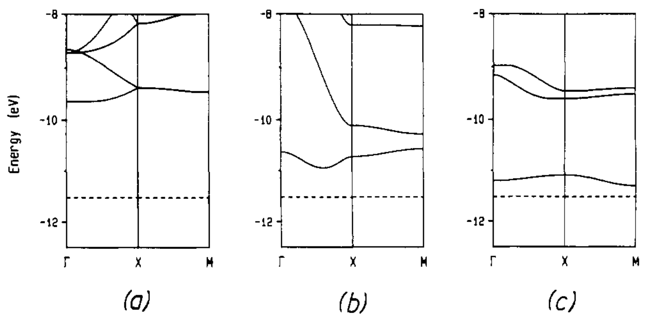

Figure 2. Band electronic structures calculated for the $(Tl_{0.5}Pb_{0.5})O_3$ layer with the A–O_{eq} sheet patterns of (a) **5a**, (b) **5b**, and (c) **5c**. The dashed line refers to the Fermi level of the half-filled CuO_2 layer $x^2 - y^2$ bands. In units of the reciprocal vectors **a*** and **b***, the wave vector points Γ, X, and M are given as follows: $\Gamma = (0,0)$, $X = (\mathbf{a}^*/2, 0)$, and $M = (\mathbf{a}^*/2, \mathbf{b}^*/2)$.

Parts a–c of Figure 2 show the band electronic structures calculated for the AO_3 layers ($A = Tl_{0.5}Pb_{0.5}$) having the A–O_{eq} sheet patterns **5a–c**, respectively, where all the bands have the Pb character. The bands having the Tl character lie above these Pb bands, and are not shown. In all three cases, the 6s-block bands of both Tl and Pb lie above the Fermi level. In agreement with the results of the molecular orbital calculations on the AO_6 octahedra, therefore, the oxidation states of Tl and Pb in $(Tl_{0.5}Pb_{0.5})Sr_2Ca_{n-1}Cu_nO_{2n+3}$ are expected to be +3 and +4, respectively. This conclusion is supported by the recent X-ray absorption study,[8] which showed that the X-ray absorption near-edge spectra of $(Tl_{0.5}Pb_{0.5})Sr_2Ca_{n-1}Cu_nO_{2n+3}$ ($n = 2, 3$) are consistent with formal oxidation states of +4 and +3 for Pb and Tl, respectively.

Parts a–c of Figure 3 show the band electronic structures calculated for the AO_3 layers ($A = Tl_{0.5}Bi_{0.5}$) with the A–O_{eq} sheet patterns **5a–c**, respectively, where all the bands have the Bi character. The bands having the Tl character lie above these Bi bands, and are not shown. In all cases the Tl 6s-block bands lie above the Fermi level. For patterns **5a,b**, the Bi 6s-block bands lie above and below the Fermi level, respectively. With the A–O_{eq} sheet pattern **5c**, the only occupied 6s-block band originates from the Bi sites with four long Bi–O_{eq} bonds. Therefore, in $(Tl_{0.5}Bi_{0.5})Sr_2Ca_{n-1}Cu_nO_{2n+3}$, the Tl oxidation state is expected to be +3. The Bi oxidation state is expected to be +3 in the most favorable case, when Bi is surrounded by four long Bi–O_{eq} bonds but +5 in other cases.

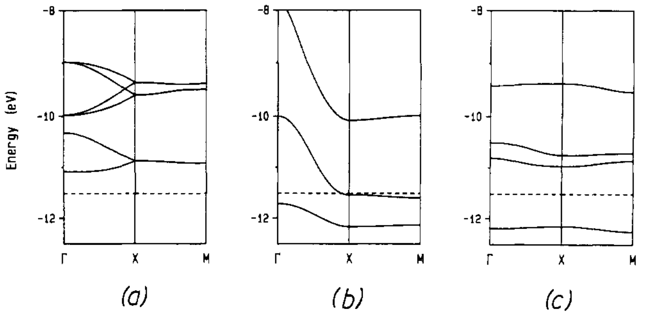

Figure 3. Band electronic structures calculated for the $(Tl_{0.5}Bi_{0.5})O_3$ layer with the A–O_{eq} sheet patterns of (a) **5a**, (b) **5b**, and (c) **5c**.

Discussion and Concluding Remarks

The oxidation state of the copper atom in the stoichiometric series $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ can be written as $Cu^{3+}(Cu^{2+})_{n-1}$, given the usual oxidation states of other elements. Since the most likely oxidation state of Pb is +4 in $(Tl_{0.5}Pb_{0.5})Sr_2Ca_{n-1}Cu_nO_{2n+3}$, the copper oxidation state of this compound is given by $Cu^{2.5+}(Cu^{2+})_{n-1}$. The copper oxidation state of $(Tl_{0.5}Bi_{0.5})Sr_2Ca_{n-1}Cu_nO_{2n+3}$ is also written as $Cu^{2.5+}(Cu^{2+})_{n-1}$ if the average oxidation state of Bi is +4. According to our study, this is possible via the Bi^{3+}/Bi^{5+} mixed valence, provided that half the Bi atoms of the $(Tl_{0.5}Bi_{0.5})O_3$ layer are at the sites with four long Bi–O_{eq} bonds. In such a case, $(Tl_{0.5}Pb_{0.5})Sr_2CaCu_2O_7$ and $(Tl_{0.5}Bi_{0.5})Sr_2CaCu_2O_7$ would have similar hole densities (n_H) in their CuO_2 layers, and hence would have similar T_c values according to the empirical relationship $T_c \propto n_H$ (underdoped region).[9] In fact, the two compounds have similar T_c values (i.e., 82 vs 90 K).[2,3] It will be of interest to experimentally verify the presence of Bi^{3+}/Bi^{5+} mixed valence in $(Tl_{0.5}Bi_{0.5})Sr_2CaCu_2O_7$. Finally we note that the Pb and Bi atoms of $ASr_2Ca_{n-1}Cu_nO_{2n+3}$ reduce the average oxidation state of Cu with respect to that in $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$. This result supports the experimental deduction[3] that the Pb and Bi atoms in the Sr-containing copper oxide superconductors play the role of lowering the copper oxidation state, thereby stabilizing the phases.

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