Gold Valence in $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ by XPS and XANES Spectroscopy

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The oxidation state of Au in AuI_3 intercalated into the interlayer space of $Bi_2Sr_2CaCuO_2O_y$ high T_c superconducting phase still remains unconfirmed due to lack of unequivocal experimental evidence, although recent theoretical studies revealed the $+1$ oxidation state of Au in the form of AuI_3^{2-} (Munzarova and Hoffmann, *J. Am. Chem. Soc.* **2002,** *124,* 5542). Here, we report the clear experimental evidences on the presence of AuI_3^{2-} through Au L_3- and I L_1-edge XANES spectroscopic studies. The Au L_3-edge XANES spectrum of $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ undoubtedly shows that its adsorption edge energy is very close to that of AuI. Furthermore, the coordination of Au^{1+} with I^{-1} in the D_{3h} symmetry is well supported by the absence of any white line feature in the I L_1-edge XANES spectrum.

Over the past decade, there have been made fruitful research efforts in our group toward the intercalation of layered high−T_c superconductor, $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ ($n = 1$, 2, and 3), where it was clearly demonstrated that various molecular species or extended lattice (I_3, Ag_xI_w, HgI_2, $HgBr_2$, $[C_5H_5N-C_nH_{2n+1}]_2$-HgI_4, or AuI_3) could intercalate between the Bi_2O_2 double layers of the above Aurivilius derivative cuprate.[1,2] Systematic characterizations on the intercalates having different basal spacing increments (Δd), and superconducting behaviors (ΔT_c)[3] allowed us to understand that the superconductivity of Bi cuprate is modulated by the oxidation level of the CuO_2 layer.[1] From another viewpoint of intracrystalline structure, the guest species were stabilized as their predominant forms of the respective reaction conditions, which highlighted the ability of intercalation reaction to realize novel heterostructures or abnormal chemical states.[1,2] In particular, $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ features an extraordinary AuI_3 molecule which is interesting not only in the formation itself but also in its D_{3h} symmetry.[2] Several computational studies examined the thermodynamic stability of AuI_3 for various geometries both in the unbound state and in $Bi_2Sr_2CaCu_2O_y$ lattice.[4−6] To summarize the results therein, free AuI_3 is prone to the Jahn−Teller distortion to a C_{2v} structure, but the intercalated AuI_3 is predicted to adopt C_{2v} or D_{3h} symmetries depending on the overall molecular charge. In this regard, we provide here the experimental results on the oxidation states of Au and I in $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ to help understand the occurrence of the unusual AuI_3 structure.

The oxidation states of Au and Bi in $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ were investigated by Au 4f X-ray photoelectron spectroscopy (XPS)[7] and X-ray absorption near edge structure (XANES) spectroscopy[8] at the Au L_3- and I L_1-edges. The XPS binding energy is mostly determined by the oxidation state of the studied atom but is also very sensitive to its chemical environment. Among the analogous compounds in which Au is bonded to Cl, Br, or I, the $4f_{7/2}$ level energy difference between the Au^{3+} and Au^{1+} decreases in parallel with the electronegativity of halide ligand. Particularly in the compounds containing Au−I bonding moiety, the Au $4f_{7/2}$ core level energies for Au^{1+} and
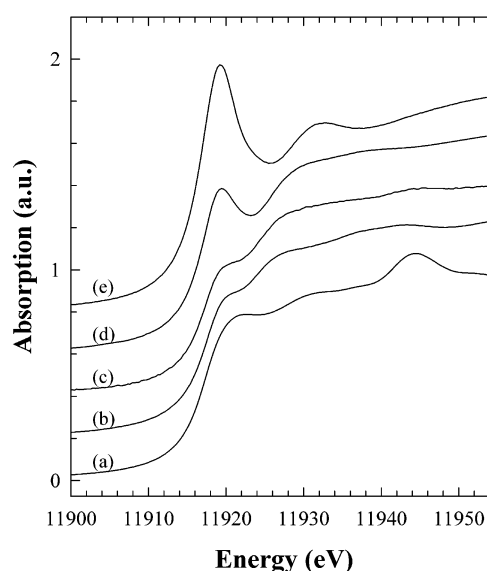
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Figure 1. Au L_3-edge XANES spectra for (a) Au, (b) AuI, (c) $(AuI_3)_{0.25}$-$Bi_2Sr_2CaCu_2O_y$, (d) $KAuI_4$, and (e) $HAuCl_4$.

Au^{3+} have been reported as 84.3∼85.0 eV and 84.3∼85.5 eV, respectively.[9,10] Such a small energy separation should be attributed to the charge transfer interaction between Au and I, arising from their similar electronegativity values (2.54 and 2.66, respectively, according to the Pauling scale[11]). From the measurements of Au 4f XPS spectra for $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ and AuI, the Au $4f_{7/2}$ XPS peaks were observed similarly at ∼84.6 eV,[12] which is significantly distinct from that for elemental Au (84.0 ± 0.2 eV)[13] and falls in the range of literature values for Au^{1+} or Au^{3+}. Commonly in the two compounds, AuI and $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$, gold interacts almost exclusively with iodine, and is expected to have similar extents of ionicity. Such similarity in bonding environments and the 4f binding energies reasonably suggest that the intercalated Au has an electronic structure very similar to that of AuI. Although the present XPS analyses cannot provide definite information due to the inherent limitation in the method and/or the unavailability of appropriate reference compounds, it is

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Figure 2. Deconvolution of the Au L_3-edge XANES spectra for Au, AuI, $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$, $KAuI_4$, and $HAuCl_4$, showing the experimental data (open circles) with the fitted preedge peak, absorption edge, and their sum.

highly probable that Au in $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ has the valence of +1 as in AuI.

The Au L_3-edge XANES spectroscopy was found to be more effective in determining the Au valence in $(AuI_3)_{0.25}Bi_2Sr_2$-$CaCu_2O_y$, presenting the spectral features corresponding to the electronic transitions from $2p_{3/2}$ to various final states. Figure 1 shows the Au L_3-edge XANES spectrum for $(AuI_3)_{0.25}Bi_2$-$Sr_2CaCu_2O_y$ and those for the reference compounds, Au(I)I, KAu(III)I$_4$, HAu(III)Cl$_4$, and Au. First of all, the oxidation state of Au in a given compound can be presumed by the edge shape, where the common oxidation states of Au (Au^0, Au^{1+}, and Au^{3+}) are easily distinguishable. Metallic gold is characterized by the broad peak in the energy region of ~11945 eV that is retained even when the metal particle size is as small as 10 Å in diameter. Spectra for the Au^{3+} ions with electronic configuration of $5d^8$ show prominent spikes on the edge rise that may be assigned to a $2p_{3/2} \rightarrow 5d$ transition. The spectrum of $(AuI_3)_{0.25}Bi_2Sr_2$-

$CaCu_2O_y$ is rather featureless by comparison, but one can easily recognize its resemblance to that of AuI.

In the interpretation of XANES spectra, it is not always necessary to identify all the detected transitions, but often the main concern is to analyze the absorption edge and the preedge peak arising from the excitations to the continuum level and the empty valence level, respectively. Although the compounds in Figure 1 contain Au ions with different valences, the expected absorption edge shifts are not readily observed because of the preedge feature resulting from the $5d-6s$ orbital mixing. According to the dipole selection rule, $\Delta l = \pm1$, the Au $2p_{3/2}$ electron can be excited to the bound states of $6s$ or $5d$, but the $2p_{3/2} \rightarrow 6s$ transition is hardly observed because of the small spatial overlap between the $2p$ and $6s$ orbitals. And, from the formal electronic configurations for the Au oxidation states, Au^0 $(5d^{10}6s^1)$, Au^{1+} $(5d^{10}6s^0)$, and Au^{3+} $(5d^86s^0)$, it is supposed that only the Au^{3+} can exhibit the $2p_{3/2} \rightarrow 5d$ transition. However,

TABLE 1: Least-Squares Fit Parameters for the Normalized Au L$_3$-edge XANES Spectra

compound	$A_B{}^a$	E_B (eV)^b	E_C (eV)^b
Au	1.82	11919.6	11920.9
AuI	1.83	11919.4	11921.8
$(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$	2.11	11919.1	11922.0
KAuI$_4$	3.63	11919.3	11923.9
HAuCl$_4$	6.18	11919.3	11925.9

^{a} A_B is preedge peak area, in (XANES unit × eV). ^{b} E_B and E_C are the energy positions of the transitions to the bound and continuum states, respectively.

in an actual situation, the proximity between the Au 5d and 6s levels can cause the orbital mixing and the d-orbital vacancy even in Au^0 or Au^{1+} states, allowing the $2p_{3/2} \rightarrow 5d$ transition.[14] Therefore, for the detailed information on the electronic structure of the above compounds, each XANES spectrum was deconvoluted into the Voigt type preedge peak and the absorption edge with an arctangent form (Figure 2).[15] The least-squares fit parameters given in Table 1 can be used to determine the relative amount of the Au 5d orbital vacancy and the energy positions of $2p_{3/2} \rightarrow 5d$ and $2p_{3/2} \rightarrow$ continuum transitions. The preedge peak position, E_B, is not likely to vary with the Au oxidation state, and the peak area, A_B, is not expected to reveal the quantitative 5d population because of the aforementioned 5d−6s interaction. However, the absorption edge energy, E_C, would reflect the total valence electron count in the Au 5d and 6s orbitals and can be a good measure of the Au oxidation state. Among the four reference compounds, it is evident that the edge energy increases consistently with the formal oxidation number of Au, while the E_C of $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ is found to be very close to that of AuI. It is therefore clear that the $(AuI_3)_{0.25}$-$Bi_2Sr_2CaCu_2O_y$ contains the Au^{1+} ion, as implied by the fingerprint investigations using the XANES and the Au 4f XPS. It is also noteworthy that the bond ionicity plays a substantial role in the apparent Au oxidation state, as shown from the E_Cs for KAuI$_4$ and HAuCl$_4$. Comparing the four compounds, Au, AuI, $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$, and KAuI$_4$, the Au L$_3$-edge energy shifts by ~1.0 eV per unit change in valence.

The I L$_1$-edge XANES spectrum of $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ was investigated in comparison with those of reference compounds I$_2$, IBi$_2$Sr$_2$CaCuO$_y$, KIO$_3$, and KIO$_4$. As well established, the preedge peak at ~5186 eV in the I L$_1$-edge XANES spectrum quantitatively reflects the 5p hole density and thereby the oxidation state of I.[1a,f] In case of $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$, no white line feature was observed,[12] indicating that the interlayer Au^{1+} ions are coordinated by I^{-1} ions. Namely, the intercalated species is described as AuI$_3{}^{-2}$, which would apparently prefer the D_{3h} symmetry as pointed out by Munzarová and Hoffmann.[6] It is thought that the facile orbital hybridization between Au and Bi enabled such an electron rich

molecule, AuI$_3{}^{-2}$, and consequently substantial electronic interactions within the host−guest complex that are evidenced by the smaller Δd and the higher deintercalation temperature of $(AuI_3)_{0.25}Bi_2Sr_2CaCu_2O_y$ compared with IBi$_2$Sr$_2$CaCu$_2$O$_y$.[2,12]

Supporting Information Available: Au 4f XPS and I L_1 XANES spectra and the thermogravimetry profiles of $(AuI_3)_{0.25}$-Bi$_2$Sr$_2$CaCu$_2$O$_y$ and reference compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) XPS spectra were collected in a VSW Scientific spectrometer with a base pressure of 2.2×10^{-9} Torr using Al Kα X-ray. C 1s core level line (284.6 eV) was used for the energy correction.

(8) X-ray absorption experiments were performed with the X-ray facility at the beam line 10B of the Photon Factory (Tsukuba) running at 2.5 GeV with a stored ring current of ~350 mA. The polycrystalline samples were homogenized with boron nitride and pressed to a pellet with an adjusted thickness for optimum edge jump ($\Delta\mu_t \approx 1$). All the data were recorded with a spacing of ~1.5 eV in a transmission mode at room temperature. From the raw data, inherent background was extracted by fitting a polynomial to the preedge region and extrapolating through the entire spectrum. After background subtraction, the resulting spectrum, $\mu(E)$, was normalized to an edge jump of unity for comparing the XANES features directly with one another.

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