Soft-x-ray absorption spectroscopy of heterostructured high-$T_c$ superconducting nanohybrids: 
$X$-Bi$_2$Sr$_2$CaCu$_2$O$_8$ [X=I, HgI$_2$, and (Py-CH$_3$)$_2$HgI$_4$]

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Unoccupied electronic states of $X$-Bi$_2$Sr$_2$CaCu$_2$O$_8$ [X-Bi2212, X=I, HgI$_2$, and (Py-CH$_3$)$_2$HgI$_4$, Py = pyridine] have been probed by O K-edge and Cu L-edge x-ray absorption near-edge structure (XANES) spectra using a bulk-sensitive x-ray-fluorescence-yield technique. In the O 1$s$ absorption edge of X-Bi2212, the pre-edge feature at $\sim$528.3 eV is attributed to transitions into O 2$p$ hole states located in the CuO$_2$ planes. As deduced from O K-edge and Cu L-edge x-ray absorption spectra, the hole concentration in the CuO$_2$ planes of X-Bi2212 increases for X=I and HgI$_2$, but decreases for X=(Py-CH$_3$)$_2$HgI$_4$, relative to pristine Bi2212. The present XANES results clearly demonstrate that the hole density within the CuO$_2$ planes of intercalated Bi$_2$Sr$_2$CaCu$_2$O$_8$ can be not only decreased but also increased, depending on the chemical character of the intercalants.

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Several techniques have been widely utilized to estimate the hole concentration for cuprate superconductors, including the Hall coefficient measurement, calculation of the bond-valence sum, 16 iodometric titration, 17,18 soft-x-ray absorption spectroscopy, 18,19 and thermoelectric power measurement. 20 Among them, soft-x-ray absorption spectroscopy using synchrotron radiation offers advantages over other measurements. The x-ray absorption near-edge structure (XANES) spectrum at the O K-edge and Cu L$_{3,2}$-edge directly probes the local concentration of hole carriers at distinct oxygen and copper sites in superconductive cuprate materials. 18

Based on extended x-ray absorption fine-structure (EXAFS) measurements at the Bi I L$_{3,2}$-edge, Cu K-edge, I L$_{3,2}$-edge, and Hg L$_{3,2}$-edge for Bi2212, HgI$_2$-Bi2212, and (Me$_3$S)$_2$HgI$_4$-Bi2212, it has been proposed that the $T_c$ evolution of Bi2212 and its intercalates is related mainly to the variation of the hole concentration in the CuO$_2$ planes. 12 To understand further the mechanism of high-$T_c$ superconductivity, it is crucially important to probe directly the hole density of intercalated cuprates with various interlayer distances. In this study, the unoccupied electronic states for Bi2212 and X-Bi2212 [X=I, HgI$_2$, and (Py-CH$_3$)$_2$HgI$_4$] have been probed by O K-edge and Cu L-edge x-ray absorption spectra using a bulk-sensitive x-ray fluorescence yield. Our XANES results demonstrate clearly that the hole density in the CuO$_2$ planes of intercalated Bi$_2$Sr$_2$CaCu$_2$O$_8$ can be both decreased and increased, depending on the chemical character of the intercalants.

II. EXPERIMENTS

The polycrystalline Bi2212 compound was prepared through conventional solid-state reaction. Detailed procedures for preparing superconducting X-Bi$_2$Sr$_2$CaCu$_2$O$_8$ [X =I, HgI$_2$, and (Py-CH$_3$)$_2$HgI$_4$] are reported elsewhere. 11,12 In brief, I- and HgI$_2$-intercalated Bi2212 compounds were prepared on heating the pristine materials and the guest iodine.
FIG. 1. O K-edge x-ray-fluorescence-yield absorption spectra of I-Bi2212, Hgl₂-Bi2212, Bi2212, and (Py-CH₃)₂Hgl₄-Bi2212.

or Hgl₂, respectively, in a Pyrex tube sealed under vacuum. Intercalation of the organic molecules was performed through the solvent-mediated reaction between Hgl₂-intercalated Bi2212 and methyl-pyridinium iodide. As verified by powder x-ray diffraction (XRD) analysis and high-resolution electron-microscopy (HREM) images, all samples for the present work are single phase.11

X-ray absorption measurements were performed at the 6-m high-energy spherical-grating-monochromator (HSGM) beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. X-ray absorption spectra were recorded in the x-ray-fluorescence-yield mode using a microchannel plate detector. The x-ray-fluorescence-yield measurement is sensitive strictly to the bulk of a sample because the probing depth is hundreds of nm. The fluorescence detector was oriented parallel to the sample surface. Photons were incident at an angle 45° with respect to the sample normal. The incident photon flux \( I_0 \) was monitored simultaneously with an Au mesh located after the exit slit of the monochromator. The x-ray-fluorescence-yield absorption spectra were corrected for both the energy-dependent incident photon intensity and the self-absorption effects, and normalized to a tabulated standard absorption cross section in the energy range 600–620 eV at the O K-edge and 1000–1020 eV at the Cu L₂,₃-edge. The photon energies were calibrated with an accuracy 0.1 eV using the known O K-edge absorption feature at 530.1 eV and the Cu L₃ white line at 931.2 eV of a CuO reference. The monochromator resolution was set at \( \sim 0.22 \) eV and \( \sim 0.45 \) eV at the O K-edge and Cu L₂,₃-edge, respectively.

III. RESULTS AND DISCUSSION

In Fig. 1, the O K-edge x-ray absorption spectra for Bi2212 and X-Bi2212 [X=I, Hgl₂, and \((\text{Py-CH}_3)_2\text{Hgl}_4\)] are depicted. The core-hole effect in the O K-edge absorption spectrum can be neglected, because of the strong similarity of O 1s absorption edges and resonant inverse photoemission spectra of Bi2212.21 The O K-edge absorption spectrum thus probes the local unoccupied density of states with \( p \) symmetry at the O sites. Based on polarization-dependent O K-edge x-ray absorption spectra of pristine Bi2212 and Hgl₂-Bi2212 single crystals, the pre-edge peak at \( \sim 528.3 \) eV in Fig. 1 has mainly O 2\( p_{x3} \) symmetry and is ascribed to holes in the single band formed on \( p \)-type doping in the CuO₂ planes, i.e., the Zhang-Rice (ZR) states.22–24 A similar feature has been characterized for many other \( p \)-type doped superconductive cuprates.25–27 The feature at \( \sim 530.5 \) eV is due to overlapping of wide antibonding Bi 6\( p \)-O 2\( p \) and the upper Hubbard band (UHB).18,19 The absorption energy of the ZR band slightly decreases with increasing intensity of the ZR band. This effect demonstrates that the Fermi level is shifted to lower energy when the hole concentration within the CuO₂ planes increases.

To quantify the results in Fig. 1, we analyzed the spectral weight of pre-edge features by fitting with Gaussian functions. The energy shift of ZR bands upon intercalation in Bi2212 was taken into consideration. The resulting hole content in the CuO₂ planes as a function of interlayer distance between the CuO₂ planes in adjacent blocks of pristine Bi2212 and various intercalates is shown in Fig. 2. As is discernible from Fig. 2, the hole concentration in the CuO₂ planes of X-Bi2212 increases for \( X \) altering from Hgl₂ to I, but decreases for \( X=(\text{Py-CH}_3)_2\text{Hgl}_4 \), relative to pristine Bi2212. As noted, the variation of hole concentration in the CuO₂ planes of X-Bi2212 is insensitive to the interlayer distance between the CuO₂ planes. The present XANES results demonstrate clearly that the CuO₂ plane hole concentration of intercalated Bi2212 can be not only decreased but also increased, depending on the chemical nature of the intercalants.

Organic or inorganic molecules become intercalated between Bi₂O₃ layers in Bi2212.11 Hence, in these intercalated Bi-based cuprates, the Bi-O plane directly faces the intercal-
ant layer. It is generally believed that hole doping of the 
CuO$_2$ planes in Bi2212 reflects charge transfer from the 
CuO$_2$ planes to the BiO planes through internal redox equi-
librium Bi(III) + Cu(II) \rightarrow Bi(III-e) + Cu(II+e).$^{12,19}$ Accordingly, the hole density in the CuO$_2$ plane is modified by the redox of the Bi-O layer in close contact with the intercalated guests. The chemical interaction between host and guest of intercalated Bi2212 is primarily affected by the relative elec-
tron donating or accepting ability involving the orbitals of 
Bi-O layers and guest molecules. Calculations based on the 
extended Hückel tight-binding band method have determined 
the relative energy levels of molecular orbitals in the Bi$_2$O$_4$$^{2-}$ cluster, Hgl$_2$, and Hgl$_2$.$^{12}$ For Hgl$_2$-intercalated Bi2212, the 
HOMO of Bi$_2$O$_4$$^{2-}$ acts as a donor orbital and the LUMO of 
Hgl$_2$ as an acceptor orbital. Electrons are thereby preferably 
transferred from the Bi$_2$O$_4$$^{2-}$ cluster to the Hgl$_2$ layer upon 
intercalation, and in turn the Bi-O layer becomes slightly 
oxidized. In contrast, for Hgl$_2$-intercalated Bi2212, the 
HOMO of Hgl$_2$$^{2-}$ behaves as a donor orbital and the LUMO of 
Bi$_2$O$_4$$^{2-}$ as an acceptor orbital, leading to partial electron 
transfer from the Hgl$_2$ anion to a Bi$_2$O$_4$$^{2-}$ cluster, i.e., to the 
Bi-O sheet. Such theoretical predictions are consistent with 
the present O K-edge XANES spectra.

If the $T_c$ variation of pristine Bi2212 upon intercalation is 
attributed to a weakening of interblock coupling due to the 
basal increment, $T_c$ is expected to decrease monotonically 
with increasing basal increment regardless of the hole 
concentration.$^{13}$ However, in contrast to theoretical prediction, 
relative to pristine Bi2212, the onset $T_c$ value increases 
slightly despite a basal increment ($\Delta d$=10.9 Å) upon (Py-
CH$_3$)$_2$Hgl$_2$ intercalation, whereas $T_c$ decreases $\sim$10 K upon 
intercalation of Hgl$_2$ ($\Delta d=7.2$ Å) and by $\sim$15 K upon in-
tercalation of iodine ($\Delta d=3.6$ Å).$^{11,12}$ It has been shown that 

$T_c$ as a function of hole concentration in the CuO$_2$ planes 
conforms to a parabolic curve for many $p$-type high-$T_c$ cu-
icate superconductors.$^{28}$ Bi$_2$Sr$_2$CaCu$_2$O$_8$ is situated in the 
overdoped region in which an increased hole concentration in 
the CuO$_2$ planes produces a decreased $T_c.$$^{18}$ Thus Hgl$_2$-
and I-intercalated Bi2212 depress $T_c$, for overdoped pristines, 
corresponding to the hole doping from intercalant layers to 
CuO$_2$ sheets. In contrast, the $T_c$ recovery upon (Py-
CH$_3$)$_2$Hgl$_2$ intercalation is attributed to a decreased hole 
density in the CuO$_2$ planes upon attaining an optimum hole 
concentration, originating from charge transfer from intercalant 
sheets to the CuO$_2$ layer in host materials. Our present 
XANES results clearly demonstrate that the variation of hole 
concentration in the CuO$_2$ planes is primarily responsible for 
the variation of $T_c$ upon intercalation.

In Fig. 3, the Cu L$_{2,3}$-edge x-ray-fluorescence-yield 
absorption spectra of pristine Bi2212 and X-Bi2212 [X=I, 
Hgl$_2$, and (Py-CH$_3$)$_2$Hgl$_2$] in the energy range 925 - 960 eV 
are reproduced. As noted, the Cu L-edge absorption spectrum 
exhibits an asymmetric profile with a tail extending to higher 
energies. Two excitonic features centered at $\sim$931.2 eV and 
$\sim$951.2 eV are ascribed to transitions from the 
Cu(2p$_{3/2,1/2}$)3d$^9$–O 2p$^6$ ground state (formally Cu$^{2+}$) into the 
Cu(2p$_{3/2,1/2}$)3d$^{10}$–O 2p$^6$ excited state, in which (2p$_{3/2,1/2}$)$^{-1}$ 
represents a 2p$_{3/2}$ or 2p$_{1/2}$ hole. The high-energy shoulders in 
Fig. 3 originating from O 2p hole states are ascribed to trans-
itions from the Cu(2p$_{3/2,1/2}$)3d$^9$L ground state into the 
Cu(2p$_{3/2,1/2}$)$^{-1}$3d$^{10}$L excited state (formally Cu$^{3+}$), with L 
denoting a ligand hole in the O 2p orbital.$^{18,29-32}$

We analyzed the absorption spectra in Fig. 3 by fitting the 
Cu L$_1$ peak and its shoulder with Gaussian functions. The 
inTEGRATED intensity of the shoulder I(Cu$^{3+}$) is normalized 
against the sum of integrated intensity of the main feature 
I(Cu$^{2+}$) and that of the shoulder itself. The normalized inten-
sity of the shoulder, i.e., I(Cu$^{3+}$)/(I(Cu$^{2+}$)+I(Cu$^{3+}$)), enables 
an estimate of the hole concentration in the CuO$_2$ planes, like 
the pre-edge peak at $\sim$528.3 eV observed in the O K-edge 
x-ray absorption spectrum.$^{29}$ In Fig. 4, the obtained normal-
ized intensity of the shoulder is plotted as a function of interlayer distance between the CuO$_2$ planes in adjacent blocks of pristine Bi$_{2212}$ and various intercalates. The normalized intensity of the shoulder increases upon intercalation with HgI$_2$ and iodine and decreases after intercalation with (Py-CH$_3$)$_2$HgI$_4$ into Bi$_{2212}$. This result is consistent with O K-edge absorption spectra in Fig. 1.

IV. CONCLUSION

We have investigated the variation of hole density of Bi$_{2212}$ and X-Bi$_{2212}$ [X=I, HgI$_2$, and (Py-CH$_3$)$_2$HgI$_4$] with high-resolution O K-edge and Cu L-edge x-ray absorption spectra. Relative to pristine Bi$_{2212}$, the hole concentration in the CuO$_2$ planes for I- and HgI$_2$-intercalated Bi$_{2212}$ increases, decreasing $T_c$ through overdoping of holes in the CuO$_2$ planes. The recovery of $T_c$ upon intercalation of (Py-CH$_3$)$_2$HgI$_4$ into Bi$_{2212}$ is ascribed to a decreased hole concentration in the CuO$_2$ planes upon attaining an optimum hole concentration. The present XANES results demonstrate clearly that the hole density within the CuO$_2$ planes of intercalated Bi$_2$Sr$_2$CaCu$_2$O$_8$ can be both decreased and increased, depending on the chemical character of the intercalants. The variation of CuO$_2$-plane hole concentration of Bi$_{2212}$ is primarily responsible for the $T_c$ variation upon intercalation.

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