

Hole states of X-Bi₂Sr₂CaCu₂O₈ [X=I, HgI₂, and (Py-CH₃)₂HgI₄] probed by O K-edge X-ray absorption spectroscopy

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Abstract

Hole states of X-Bi₂Sr₂CaCu₂O₈ [X=I, HgI₂, and (Py-CH₃)₂HgI₄, Py = pyridine] have been probed by O K-edge X-ray absorption near-edge structure (XANES) spectra. In the O 1s absorption edge of X-Bi2212, the pre-edge peak at ~528.3 eV is attributed to transitions into the O 2p hole states located in the CuO₂ planes. The hole concentration in the CuO₂ planes of X-Bi2212 increases for X=I and HgI₂, but decreases for X= (Py-CH₃)₂HgI₄ as compared to pristine Bi2212. The variation of CuO₂-plane hole concentration of Bi2212 is primarily responsible for the *T_c* variation upon intercalation.

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1. Introduction

The intercalation of guest molecules into the high-*T_c* superconductive cuprate materials has received considerable attention recently due to practical applications of high-*T_c* superconductors [1,2]. Several new high-*T_c* intercalated cuprate superconductors, such as La₂CuO_{4-δ}F_y [3,4], Sr₂CuO₂F_{2+δ} [5], HgBa₂Sr₂Cu₂(CO₃)O₇ [6], (Tl_{0.5}Pb_{0.5})Sr₄Cu₂(-CO₃)O₇ [7], HgBa₂Ca_{n-1}Cu_nO_{2n+2+δ}F_y (*n*=1–3) [8] and X-Bi₂Sr₂Ca_{m-1}Cu_mO_y [*m*=1 and 2; X-Bi2201 and X-Bi2212; X=I, HgI₂, HgBr₂, (Me₃S)₂HgI₄, and (Py-C_nH_{2n+1})₂HgI₄, *n*=1–12, Py=pyridine], [9,10] have been reported. Among them, X-Bi2212 or X-Bi2201 systems have attracted extensive studies because of their unique properties and controversial issues regarding the role of interlayer coupling on superconductivity [9–13].

The pristine Bi2212 and Bi2201 materials exhibit weakly bound Bi₂O₂ double layers, consequently enabling the free expansion of the unit cell in the *c* direction without significantly changing other internal lattice structure. [9,10] Various inorganic or organic modulation layers were intercalated into Bi₂O₂ double layers of the Bi2201 and Bi2212 materials. In particular, long-chain organic molecules, such as (Py-C_nH_{2n+1})₂HgI₄ for *n*=1–12, were successfully

intercalated into Bi-based cuprates in the form of a complex heterostructured high-*T_c* superconducting nanohybrid. [9] Compared to the pristine Bi2212, the onset *T_c* value increases slightly in spite of basal increment ($\Delta d=10.9$ Å) upon the (Py-CH₃)₂HgI₄ intercalation, whereas *T_c* is depressed by ~10 K upon mercuric iodide intercalation ($\Delta d=7.2$ Å) and by ~15 K upon the iodine intercalation ($\Delta d=3.6$ Å). [9,10] One of the interesting issues is to elucidate the origin of the *T_c* variation through the various intercalants into Bi₂Sr₂CaCu₂O₈, because it gains profound insight into the mechanism of the appearance of high-*T_c* superconductivity. One possible origin is due to the structural change along the *c*-axis; another is ascribed to the variation of hole concentration in the CuO₂ sheets through intercalation.

It is a general consensus that the hole states play a pivotal role for superconductivity in the p-type cuprate superconductors. Therefore, understanding of the unoccupied electronic structure near the Fermi level of cuprate superconductors is an important step towards unveiling the mechanism of superconductivity. Soft-X-ray absorption spectroscopy using synchrotron radiation has been widely applied to directly probe the local density of unoccupied states at distinct oxygen and copper sites in high-*T_c* superconductors. [14] In particular, polarization-dependent X-ray absorption measurements are able to provide detailed information on the orbital character of the hole states in the p-type cuprates [15].

In this study, unoccupied electronic states near the Fermi level for Bi2212 and X-Bi2212 [X=I, HgI₂, and (Py-CH₃)₂HgI₄] have been probed by O K-edge X-ray

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absorption near edge (XANES) spectrum using a bulk-sensitive X-ray-fluorescence-yield mode. The present XANES results demonstrate clearly that the CuO_2 -plane hole density of intercalated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ can be not only reduced but also increased, depending on the chemical character of the intercalants.

2. Experiment

The polycrystalline Bi2212 compound was prepared by conventional solid-state reaction. Detailed procedures for preparing superconducting $\text{X-Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [$\text{X}=\text{I}$, HgI_2 , and $(\text{Py-CH}_3)_2\text{HgI}_4$] have been reported in detail elsewhere [9, 10]. In brief, the I- and HgI_2 -intercalated Bi2212 compounds were prepared by heating the pristine materials and the guest iodine or HgI_2 , respectively in a vacuum-sealed Pyrex tube. The intercalation of the organic molecules was carried out by the solvent-mediated reaction between HgI_2 -intercalated Bi2212 and methyl-pyridinium iodide. As checked by powder X-ray diffraction (XRD) analysis and high-resolution electron microscopy (HREM) images, all samples for the present work are single phase [9].

The X-ray absorption measurements were carried out at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan with an electron beam energy of 1.5 GeV. The synchrotron radiation was monochromatized by the 6 m high-energy spherical grating monochromator (HSGM) beamline which covers the photon energy range of 90–1400 eV. The polarization-dependent X-ray absorption spectra with various incidence angles (ϕ) with respect to the surface normal have been recorded by rotating the sample around a vertical axis. The linear polarization of the monochromatic beam was estimated to be around 97%. The X-ray-fluorescence-yield absorption spectra were obtained using a microchannel plate (MCP) detector. In contrast to the electron-yield measurements, the X-ray-fluorescence-yield measurement is a strictly bulk sensitive technique with a probing depth of thousands of angstrom. The incident photon flux (I_0) was monitored simultaneously by 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 (I_0) and the self-absorption effects, and normalized to tabulated standard absorption cross section in the energy range of 600–620 eV at the O K edge. The photon energy was calibrated with an accuracy of 0.1 eV using the known O K-edge absorption peak at 530.1 eV of a CuO reference. The monochromator resolution was set to ~ 0.22 eV at the O 1s edge. All the measurements were performed at room temperature.

3. Results and discussion

Polarization-dependent O K-edge X-ray absorption spectra of a Bi2212 single crystal recorded at different incidence angles (ϕ) are reproduced in Fig. 1 using a bulk-sensitive X-ray-fluorescence-yield mode. The absorption spectrum for $\phi=0^\circ$ corresponds to the normal incidence geometry where the

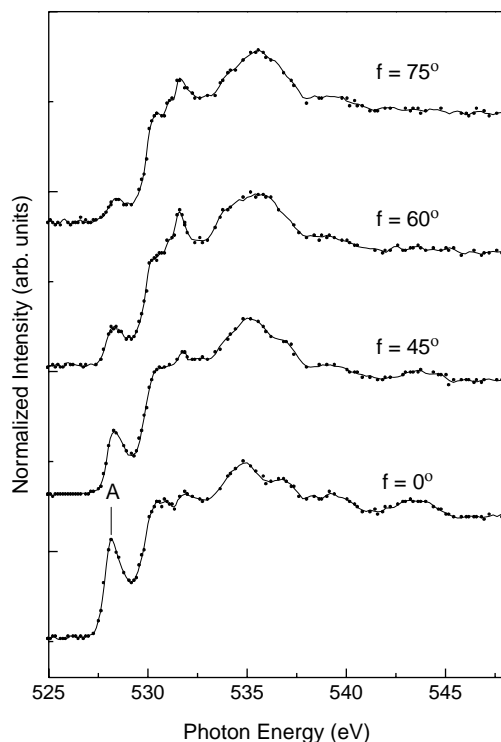


Fig. 1. Polarization-dependent O K-edge X-ray absorption spectra of the Bi2212 single crystal recorded at different incidence angles (ϕ) using a bulk-sensitive X-ray-fluorescence-yield mode.

electric field vector E of the linearly polarized synchrotron light is parallel to the ab plane of the single crystal, while spectrum for $\phi=75^\circ$ represents the grazing incidence geometry where E vector is nearly parallel to the c axis of the single crystal. It is generally believed that the core-hole effect in O K-edge absorption spectrum can be neglected, due to the strong similarity of O 1s absorption edges and resonant inverse photoemission spectra of Bi2212 [16]. Thus, the O K-edge absorption spectrum probes the local unoccupied density of states with p symmetry at the O sites.

The prominent feature in the O K-edge X-ray absorption spectrum for $E//ab$ ($\phi=0^\circ$), as shown in Fig. 1, is a pronounced pre-edge peak (labeled A) at ~ 528.3 eV. As ϕ is increased from $E//ab$ to $E//c$, spectral weight of peak A is significantly reduced. According to dipole selection rules, for $E//ab$, only the unoccupied electronic states with O $2p_{xy}$ symmetry are probed and in the $E//c$ case, the empty O $2p_z$ states are accessible for the O 1s transition. Accordingly, the pre-edge peak A has mainly O $2p_{xy}$ symmetry and is attributed to the unoccupied O $2p_{xy}$ states in the CuO_2 planes. This result agrees with that previously published in literature [17].

In Fig. 2, the O K-edge X-ray absorption spectra for polycrystalline Bi2212 and $\text{X-Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [$\text{X}=\text{I}$, HgI_2 , and $(\text{Py-CH}_3)_2\text{HgI}_4$] are depicted. As demonstrated, the pre-edge peak at ~ 528.3 eV was ascribed to the hole states in the singlet band formed on p-type doping in the CuO_2 planes i.e. the Zhang-Rice (ZR) states [17,18]. A similar feature has been characterized for many other p-type doped superconductive cuprates [19–21]. The absorption feature at ~ 530.5 eV is due to the

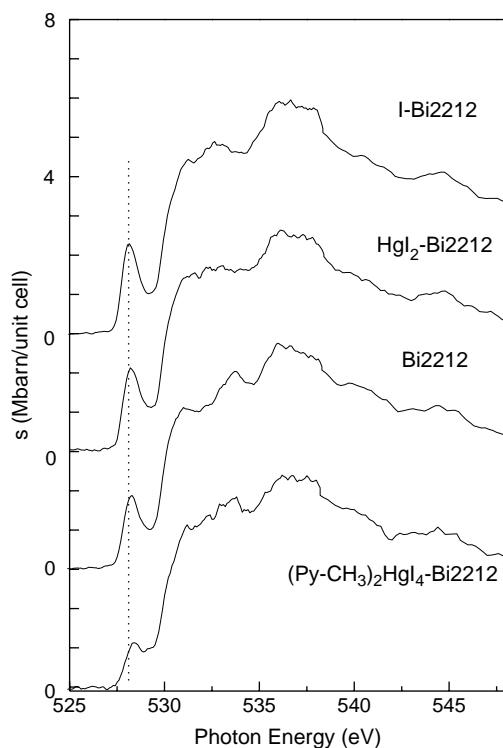


Fig. 2. O K-edge X-ray-fluorescence-yield absorption spectra of polycrystalline I-Bi2212, HgI₂-Bi2212, Bi2212, and (Py-CH₃)₂HgI₄-Bi2212.

overlapping of wide antibonding Bi6p–O2p and the upper Hubbard band (UHB) [14,15]. Due to the strong on-site correlation effects on the copper sites in the cuprate superconductors, the UHB state has always been assumed to exist. As noted from Fig. 2, the hole concentration in the CuO₂ planes of X-Bi2212 increases for X=I and HgI₂, whereas it depresses for X=(Py-CH₃)₂HgI₄, relative to pristine Bi2212. In addition, the absorption energy of the ZR band slightly decreases with increasing intensity of the ZR band. This demonstrates that the Fermi level is shifted to a lower energy when the hole concentration within the CuO₂ planes increases.

To quantify the results in Fig. 2, the spectral weight of pre-edge peaks was analyzed by fitting with Gaussian functions. The energy shift of the ZR bands upon intercalation in Bi2212 was also 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. 3. As noted, the hole concentration in the CuO₂ planes of X-Bi2212 increases when X altering from HgI₂ to I, but decreases for X=(Py-CH₃)₂HgI₄, as compared to pristine Bi2212. The present XANES results clearly demonstrate that the CuO₂-plane hole density of intercalated Bi2212 can be not only reduced but also increased, depending on the chemical nature of the intercalants. In addition, we found that the variation of spectral weight of the UHB and BiO sheets after intercalation in Bi2212 shows a trend similar to the variation of hole concentration in the ZR band (not shown).

It is well known that an increase of hole content in the CuO₂ planes of cuprate superconductors will be accompanied by the

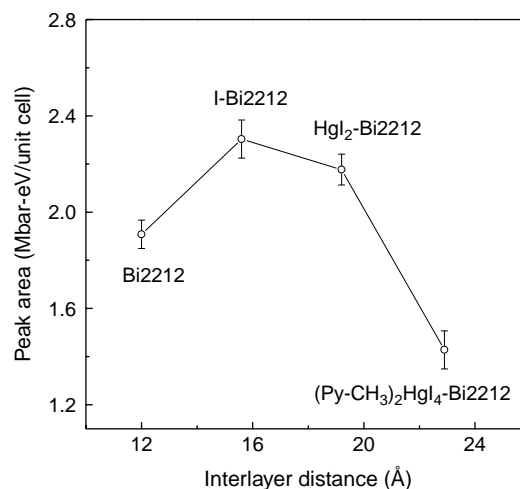


Fig. 3. Hole content in the CuO₂ planes (, i.e.528.3 eV peak) as a function of interlayer distance between the CuO₂ planes in adjacent blocks of pristine Bi2212, I-Bi2212, HgI₂-Bi2212, and (Py-CH₃)₂HgI₄-Bi2212.

expense of the UHB, due to strong correlation effects in the CuO₂ planes [22,23]. In other words, the spectral weight of the UHB is expected to conform to a trend as I-Bi2212 < HgI₂-Bi2212 < Bi2212 < (Py-CH₃)₂HgI₄-Bi2212. Thus, the hole density in the BiO planes follows this trend as I-Bi2212 > HgI₂-Bi2212 > Bi2212 > (Py-CH₃)₂HgI₄-Bi2212. Similar results were confirmed by Bi L₃-edge XANES spectra for Bi2212 and HgI₂-Bi2212 [10]. The increase of hole density in the BiO planes upon the HgI₂ or iodine intercalation into Bi2212 is an indication of increase in the valence value of bismuth [14]. It is generally believed that p-type doping of the CuO₂ planes in Bi2212 is attributed to the charge transfer from the CuO₂ planes to the BiO planes by forming electron pockets in the Bi6p–O2p band [10,15]. Accordingly, the variation of hole concentration for intercalated Bi2212 exhibits a similar trend for the CuO₂ and BiO planes.

It has been shown that the organic or inorganic molecules were intercalated into between B₂O₂ layers in Bi2212 [9]. In other words, in the intercalated Bi-based cuprates, the Bi–O plane directly faces the intercalant layer. We therefore expect the chemical interaction between host and guest of intercalated Bi2212 to be primarily affected by the relative electron donating or accepting ability involving the molecular orbitals of the Bi–O layer and guest molecules. Based on the extended Hückel tight-binding band calculation method, the relative energy levels of molecular orbitals in the Bi₂O₄²⁻ cluster, HgI₂, and HgI₄²⁻ have been determined [10]. For the HgI₂-intercalated Bi2212 cuprate, the HOMO of Bi₂O₄²⁻ acts as a donor orbital and the LUMO of HgI₂ as the acceptor orbital. Electrons are thereby preferably transferred from the Bi₂O₄²⁻ cluster to the HgI₂ layer upon intercalation, and in turn the Bi–O layer becomes slightly oxidized. In contrast, for the HgI₄²⁻ intercalated Bi2212 cuprate, the HOMO of HgI₄²⁻ behaves as the donor orbital and the LUMO of Bi₂O₄²⁻ as an acceptor orbital, leading to a partial electron transfer from HgI₄ anion to Bi₂O₄²⁻ cluster i.e. to the Bi–O sheet. Such theoretical predictions are consistent with the present O K-edge XANES spectra.

T_c as a function of CuO_2 -planes hole concentration conforms to a parabolic curve for several p-type high- T_c cuprate superconductors [24]. It has been shown that $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is situated in the overdoped region in which an increase in the CuO_2 -plane hole concentration leads to a decrease in the T_c [14]. Thus, the HgI_2 - and I-intercalated Bi2212 depress the T_c value of overdoped pristines, corresponding to the hole doping from the intercalant layers to the CuO_2 sheets. In contrast, the T_c recovery upon the $(\text{Py-CH}_3)_2\text{HgI}_4$ intercalation is attributed to the reduction of hole density in the CuO_2 planes for attaining an optimum hole concentration, originating from the charge transfer from the intercalant sheets to the CuO_2 layer in the host materials. If the T_c variation 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 [11]. The present XANES results clearly demonstrate that the variation of hole concentration in the CuO_2 planes is primarily responsible for the T_c variation upon intercalation.

4. Conclusion

We have investigated the hole-density variation of Bi2212 and X- Bi2212 [X=I, HgI_2 , and $(\text{Py-CH}_3)_2\text{HgI}_4$] by high-resolution O K-edge X-ray absorption spectra. As compared to pristine Bi2212 , the hole concentration in the CuO_2 planes for I- and HgI_2 -intercalated Bi2212 increases, leading to depress the T_c value due to overdoping of holes in the CuO_2 planes. The T_c recovery upon the $(\text{Py-CH}_3)_2\text{HgI}_4$ intercalation into Bi2212 is ascribed to the reduction of hole concentration in the CuO_2 planes for attaining an optimum hole concentration. The present XANES results clearly demonstrate that the hole density within the CuO_2 planes of intercalated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ can be not only reduced but also increased, depending on the chemical character of the intercalants. The variation of CuO_2 -plane hole concentration of Bi2212 is primarily responsible for the T_c variation upon intercalation.

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