X-ray-absorption near-edge structure study of $IBi_2Sr_2CaCu_2O_y$

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A polarization-dependent I L_1-, Cu K-, and Bi L_3-edge x-ray-absorption near-edge structure study has been carried out on both $IBi_2Sr_2CaCu_2O_y$ and $Bi_2Sr_2CaCu_2O_y$ single crystals. The I L_1-edge results indicate that the intercalated iodine layers receive electronic charges and the I $5p$-orbital holes are in states primarily oriented in the I plane. The Cu K-edge results show that the electronic structure of the CuO_2 layer is only slightly affected by the iodine intercalation. Some evidence for a small shift of the unoccupied Cu bands towards higher energy and a weakening of the ligand to Cu charge transfer is seen. These effects could nevertheless be contributing factors to the decrease of T_c. It is observed that iodine intercalation induces about 0.25 eV downward (and upward) edge shift in the Bi L_3-edge spectrum with the polarization vector $E\|c$ axis (and $E\perp c$ axis). We interpret this observation by the downward shift of the out-of-plane part and upward shift of the in-plane part of the $6d_{t_{2g}}$ and $6d_{e_g}$ states, caused by the change of the Bi—O bonding configuration from octahedral to pyramidal. Our results indicate that the Bi valence state is close to $+3$ in both $IBi_2Sr_2CaCu_2O_y$ and $Bi_2Sr_2CaCu_2O_y$ crystals but with the Bi sites manifesting a more metalliclike behavior along the c-axis direction upon iodine intercalation.

I. INTRODUCTION

The iodine-intercalated $Bi_2Sr_2CaCu_2O_y$ (Bi 2:2:1:2) compound, $IBi_2Sr_2CaCu_2O_y$ (IBi 2:2:1:2), exhibits superconductivity and an interesting anisotropic normal-state resistivity.[1,2] The metallization of the normal-state resistivity along the c axis has appeared to be a challenge to some of the theoretical models based on holon-spinon scattering.[2,3] The large-crystal expansion ($\sim 23\%$) upon iodine intercalation[1,4] has led to speculation that the interblock coupling rather than the electronic-structure change of the CuO_2 layers might be the primary source

for the decrease of T_c ($\sim 10\%$).[1,2,4] However, to our knowledge, there has been no direct electronic structure evidence that supports this speculation. Due to the virtual absence of the electronic-state information, the discussions so far have been almost solely based on the structural information about the IBi 2:2:1:2 system. The normal-state transport and the superconducting properties (e.g., T_c) are closely related to the electronic parameters, such as the Cu valence state, the nature and concentration of the carriers, the state density near the Fermi level, and the internal charge-transfer processes.[5,6] Thus, electronic-structure experiments selectively probing the

iodine, Cu-O and Bi-O layers of IBi 2:2:1:2, especially those which can distinguish between the in-plane and out-of-plane electronic states, are urgently needed.

In this paper, we present polarized I L_1-, Cu K-, and Bi L_3-edge spectra for IBi 2:2:1:2 and Bi 2:2:1:2 single crystals and unpolarized spectra for the corresponding powder samples. The purpose of this study is to probe the electronic-structure modification in Cu-O and Bi-O layers induced by iodine intercalation with particular emphasis on the in-plane versus out-of-plane electronic states around iodine, Cu, and Bi sites. Our results indicate that electronic charge has been transferred into the I $5p$ orbitals. The effective charge of the Cu and the electronic structure of the CuO$_2$ layers are only slightly affected by the insertion of iodine layers. However, the effects could be relevant to the 10-K drop in T_c. We also find anisotropic shifts of the in-plane and out-of-plane Bi $6d$ states. Specifically, the Bi L_3 spectrum for $\mathbf{E}\|c$ axis shifts to lower energy (towards the Bi L_3 spectrum of metallic Bi), suggesting that the Bi sites become more metalliclike along the c-axis direction upon iodine intercalation.

II. EXPERIMENT

The IBi$_2$Sr$_2$CaCu$_2$O$_y$ (or IBi 2:2:1:2) and pristine Bi$_2$Sr$_2$CaCu$_2$O$_y$ (or Bi 2:2:1:2) single crystals and polycrystalline samples used in this study were prepared as has been described earlier.[1,2] Samples from the same batch as those used for the present study were characterized by x-ray diffraction, transmission electron microscopy, and transport studies.[1,2,4] The single crystal and polycrystalline IBi 2:2:1:2 samples are prepared separately by iodine intercalation into single crystal and polycrystalline Bi 2:2:1:2.

The x-ray absorption measurements were carried out at the National Synchrotron Light Source on bean line X-11A for the CuK- and Bi L_3-edge measurements, and on X-19A for the I L_1-edge measurements. Si(111) double-crystal monochromator were used on both of these two beam lines. The polarized spectra for single crystals were measured using flourescence mode detection while the unpolarized spectra for powder polycrystalline samples were obtained using transmissions mode detection (for the Cu K- and Bi L_3-edge measurements) and total electron yield detection (for the I L_1-edge measurements). Energy calibration was made by simultaneously measuring the spectra of Cu$_2$O and Bi$_2$O$_3$ standards. To obtain higher signals for the single crystals, collages of similarly oriented small crystals (each about $4 \times 4 \times 0.1$ mm^3) were carefully assembled. The powder samples for transmission detection were made in the form of four to eight layers of fine powders dusted onto tape. The spectra have been normalized to unit in the continuum region.

III. RESULTS AND DISCUSSION

A. Iodine L_1-edge results

In Fig. 1 we show the L_1 edges of powder samples of I$_2$, IBi 2:2:1:2 and KIO$_3$. Also shown in the figure is the
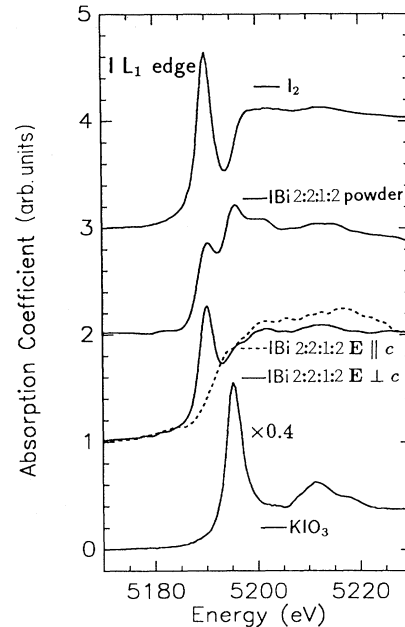

FIG. 1. The polarized I L_1-edge spectra for single crystal IBi$_2$Sr$_2$CaCu$_2$O$_y$ (IBi 2:2:1:2) together with the unpolarized spectra for powder I$_2$, IBi 2:2:1:2, and KIO$_3$ samples.

polarized I L_1 spectra for a single crystal of IBi 2:2:1:2 for the $\theta = 15°$ (or $\mathbf{E}\|c$) and $\theta = 90°$ (or $\mathbf{E}\perp c$) orientations, where θ is the angle between the x-ray polarization vector $\mathbf{E}$ and the c axis of the crystal. The extremely intense peak (located at 5195.3 eV) at the edge in KIO$_3$ is a so-called "white line" (WL) type feature, associated with transitions from the $2s$ level into $5p$ states above E_F (note the KIO$_3$ spectrum is displayed on a reduced scale). The dramatic decrease in the intensity of the WL feature between KIO$_3$ (formally with six empty p states) to I$_2$ (formally with one empty p state) should be noted. The $5p$ WL peak located at about 5190 eV in the I$_2$ spectrum is well resolved from the step feature which marks the onset of transitions into mixed $np(n > 5)$/continuum states. By fitting the I$_2$ spectrum to a superposition of an arctangent (to model the continuum onset) plus a WL feature (a Lorentzian-Gaussian combination) we have been able to determine the relative area of the WL feature to be about 6.2 eV. The unit used here for the area is defined as the product of energy in eV and the continuum step height which is normalized to unit.

Turning to the I L_1 edge of the powder IBi 2:2:1:2 in Fig. 1 the intensity of the WL feature located at 5190.2 eV can be seen to be reduced below that (located at 5190.0 eV) of I$_2$. This would support the notion that there is some transfer of charge to the I layer from other layers of the compounds. Indeed the IBi 2:2:1:2 powder spectrum is quite similar to that[7] of HgI$_2$ for which the electron transfer to the I is well accepted. It should be noted that the second peak (located at 5195.7 eV) in the spectrum of powder IBi 2:2:1:2 lies very close in energy to the intense KIO$_3$ WL. Since this powdered sample was always in powdered form (including during intercala-

tion) and since the single-crystal spectra show no such second peak we are inclined to attributed this to a small concentration of oxidized I in this powdered material.

The polarized IBi 2:2:1:2 spectra in Fig. 1 dramatically show an anisotropy in the I $5p$ hole distribution with the E⊥c spectrum exhibiting a p hole related WL feature but the E∥c spectrum exhibiting only a continuum onset feature. Using the E∥c spectrum as an estimate of the continuum onset we have estimated the area of the E⊥c WL feature to be 3.1 eV (in the same unit used in the I_2 discussion above). Assuming a linear coupling[7] of this WL area to the $5p$ hole count p and the $p = 1$ for I_2, this implies that the I $5p$ hole count for IBi 2:2:1:2 is roughly 0.5 Thus, the degree of electronic charge transfer into the I $5p$ orbitals appears to be 0.5 e^- at each I atom. The remaining localized I $5p$ orbital holes would appear to be in states oriented in the I plane. The absence of any peak in the polarized spectra in the energy region where the I^{5+} peak of KIO_3 is located suggests that iodine in IBi 2:2:1:2 crystal does not contain higher valent (close to or higher than +5) components.

B. Cu K-edge results

In Fig. 2, we present the polarized Cu K-edge spectra for the single crystals of IBi 2:2:1:2 and Bi 2:2:1:2 together with the unpolarized spectrum for an IBi 2:2:1:2 powder sample. The Cu K-edge spectrum for polarization vector E nearly parallel to the c axis ($\theta = 15°$) stands in sharp contrast with that for E perpendicular to c axis ($\theta = 90°$) spectrum. It is clear from the data that features A and B are basically associated with the E∥c spectrum and that features C and D are associated with E⊥c spec-
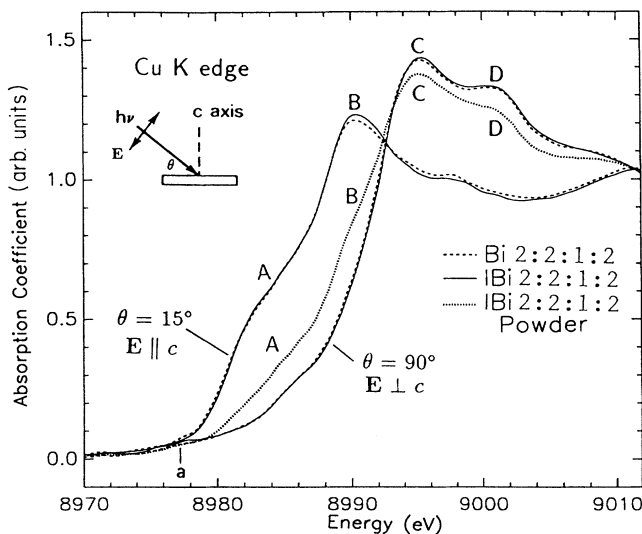
trum. These double-peak features can be interpreted in a way similar to those previously used[8,9] for the divalent cuprates Nd_2CuO_4 and Sr_2CuO_3. Features A and B in the E∥c spectrum are assigned to the 1s to out-of-plane $4p_\pi$ states transitions, whereas features C and D in the E⊥c spectrum correspond to the transitions from the 1s to the in-plane $4p_\sigma$ states. The lower-energy A and C features involve "shakedown" final states in which the core hole is better screened (relative to the B and D features) by ligand to metal charge transfer. These final states are usually denoted by $3d^{10}\underline{L}$, where $\underline{L}$ denotes a hole in the ligand shell. The small feature, a, near 8978 eV, visible in the E⊥c spectrum of the IBi 2:2:1:2 crystal, is due to quadrupolar $1s \rightarrow 3d$ transition.[8] This feature is washed out in the E∥c spectrum by the sharply rising intensity of feature A.

In order to place the IBi 2:2:1:2 materials in the context of other Cu oxides we show in Fig. 3 a comparison of the powder Cu K-edges of a series of such materials. The materials (Cu and Cu_2O) with strong d^{10}-related components are shown for reference. The Cu_2O and Cu-metal spectra clearly stand out by virtue of the strong A' feature associated with the $1s \rightarrow 4p_\pi$ transition with a $3d^{10}$ and $3d^{10}4s^1$ ground-state configuration. The absence of any A'-feature spectral weight for the IBi 2:2:1:2 material clearly place it in the class of materials with negligible $3d^{10}$ state weight (i.e., in Cu^{2+}, $d^9 - 10^{10}\underline{L}$ based materials).

In terms of the feature identifications (A through D) and their relative energies the Cu K-edge spectrum of IBi 2:2:1:2 is similar to the host of other oxide materials built upon the Cu^{2+} square planar Cu-O layer unit (see Fig. 3). It is worth pointing out that the $1s \rightarrow 4p_\pi$ shakedown feature A in the E∥c spectrum of IBi 2:2:1:2 (and Bi 2:2:1:2) is much less prominent and occurs at higher energy than in Nd_2CuO_4 (Ref. 9) (see Fig. 3). Indeed the A features have been relegated to subtle shoulder on the ini-
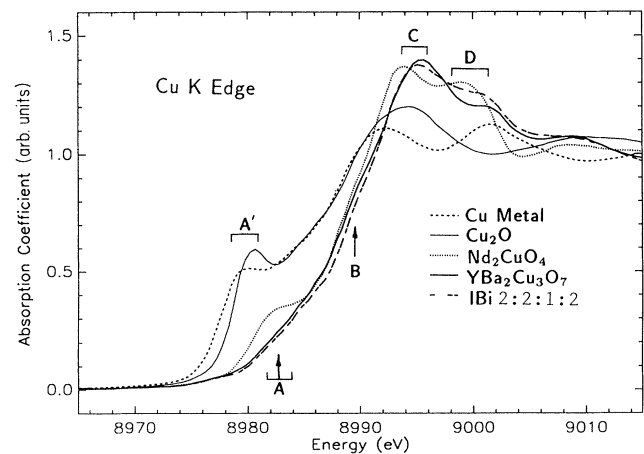

FIG. 2. Polarized Cu K-edge spectra for single crystals $IBi_2Sr_2CaCu_2O_y$ (solid curves) and $Bi_2Sr_2CaCu_2O_y$ (dashed curves) together with data for polycrystalline $IBi_2Sr_2CaCu_2O_y$ sample (dotted curve). The final states (and final d orbital configurations) associated with the feature assignments in the figure are A, $4p_\pi(d^{10}\underline{L})$; $B,4p_\pi(d^9)$; $C,4p_\sigma(d^{10}\underline{L})$; and $D,4p_\sigma(d^9)$.

FIG. 3. The Cu K near-edge spectra for powder polycrystalline $IBi_2Sr_2CaCu_2O_y$ and reference samples. The final states associated with the feature A' are $4P_\pi(3d^{10})$ for Cu_2O and $4p_\pi(3d^{10}4s^1)$ for Cu metal, respectively, while those associated with feature $A - D$ are as in Fig. 2.

tial rising portion of the edge (see Fig. 3). This intensity change in the $1s \rightarrow 4p_\pi$ transition is presumably due to the additional apical oxygen (i.e., elongated CuO_5 coordination) present in the 2:2:1:2 materials,[4,10] but absent in the Nd_2CuO_4. Simple cluster-model calculations, assuming that the Coulomb interaction energy between the Cu $1s$ hole and the Cu $3d$ hole is much larger than the $d^9 \rightarrow d^{10}\underline{L}$ charge-transfer energy V, have shown that the intensities of features A and B can be approximately proportional to the Cu-ground state $d^{10}\underline{L}$ and d^9 components.[8,11] Thus, the observed much smaller intensity of feature A in the spectrum of IBi 2:2:1:2 indicates that the average electronic charge transferred away from the Cu sites to the ligands is less in Nd_2CuO_4 than in IBi 2:2:1:2. Such a result is not surprising since the apical oxygen anion of Cu would be expected to draw additional electronic charge away from the Cu sites[8,12] and thus increase the ionicity of the Cu in the CuO_2 plane. This conclusion is consistent with those derived from the Cu $2p$ x-ray photoemission spectroscopy results, i.e., the satellite (corresponding to $3d^9$) to main peak (corresponding to $3d^{10}\underline{L}$) intensity ratio are ~ 0.28 in Nd_2CuO_4 and ~ 0.40 in Bi 2:2:1:2, respectively.[13]

The Cu valence in IBi 2:2:1:2 has been studied using the Cu K-edge measurements on powder material (see Fig. 3). The unpolarized K-edge spectrum of the IBi 2:2:1:2 (and indeed also the Bi 2:2:1:2) powder sample in Fig. 2 can be well reproduced by the combination of the polarized $E\|c$ ($\theta = 150°$) and $E\perp c$ ($\theta \approx 90°$) spectra according to formula $\sigma(\theta) = \sigma_c \cos^2(\theta) + \sigma_{ab} \sin^2(\theta)$, where $\theta = 55°$ is assumed for the powder sample and σ_c and σ_{ab} are the cross sections with **E** vector strictly along the c axis and on the ab plane, respectively. This result is consistent with the Cu K-edge result reported by Bianconi et al.[10] for IBi 2:2:1:2. In Fig. 3, Cu metal, Cu_2O, and Nd_2CuO_4 are used as Cu^0, Cu^{+1}, and Cu^{+2} references, respectively. The Cu-K absorption edge of IBi 2:2:1:2 lies at higher energy than Nd_2CuO_4 and even slightly higher energy than the well-known $YBa_2Cu_3O_7$, which has a formal valence of $Cu^{+2.33}$. This suggests that the formal Cu valence in IBi 2:2:1:2 is considerably larger than $+2$, probably even higher than the $+2.33$ in $YBa_2Cu_3O_7$. This results is consistent with our estimate[10] of the characteristic edge energy defined with the first energy moment method due to Alp et al.[14] Moreover, comparison of the $4p_\sigma$ features [$C(d^{10}\underline{L})$ and $D(d^9)$] indicates a $C \rightarrow D$ transfer of intensity on passing from $YBa_2Cu_3O_7$ to IBi 2:2:1:2. This further supports the increasing d^9 (relative to $d^{10}\underline{L}$) weight and increasing average Cu valence in the IBi 2:2:1:2 material.

We now turn our discussion to the effects of iodine intercalation on electronic structure of the CuO_2 plane. In Fig. 2, we compare the polarized Cu K-edge spectra of the pristine Bi 2:2:1:2 and intercalated IBi 2:2:1:2 single crystals. The effects of the iodine intercalation on the polarization Cu K-edge spectra can be summarized as following: first, the positions and shapes of the spectral features (A through D) are almost the same between the Bi 2:2:1:2 and IBi 2:2:1:2 crystals; second, detailed inspection of the spectra reveals that the iodine intercalation induces a slight (about 0.1 eV) edge shift toward

higher energy in the $E\perp c$ spectrum and a slight increase of the intensity of feature B in the $E\|c$ spectrum. Since the removal of a $3d$ electron on going from Cu^{+2} to Cu^{+3} usually causes a positive edge-energy shift of about 2–4 eV in the Cu K-edge[14,15] (for example, the edge-energy shift of $La_2Li_{0.5}Cu_{0.5}O_4$ relative to La_2CuO_4 is about 3 eV),[16] the small observed shift would indicate that a reduction of only about 0.03 $3d$ electrons occurs at each Cu site upon intercalation. Therefore, it is quite fair to say that the Cu valence state is almost unaffected by iodine intercalation. It is reasonable to believe that the Cu—O bonding (and thus the Cu $3d$-O $2p$ hybridization) is also almost unaffected as supported by reported constancy of the a and b lattice parameters and of the Cu-cation bonding lengths.[1,4] Thus, it can be concluded that the electronic structure of the CuO_2 layers is unaffected, to first order, by iodine intercalation. This is of course consistent with the relatively small change in T_c upon iodine intercalation.

It is worthwhile to consider second-order electronic structure origins of the small spectral differences mentioned above between Bi 2:2:1:2 and IBi 2:2:1:2. The about $+0.1$-eV shift of the $E\perp c$ spectrum of IBi 2:2:1:2 could be interpreted as due to a shift of the upper unoccupied band that consists of in-plane $4s/p$, and $3d$ (hybridized with O $2p$) states. We caution that the unoccupied Cu $3d$ band does not necessarily shift in the same manner as the in-plane Cu $4p$ band. Such an interpretation has been applied to the Cu-K edge shifts in the n-type superconductors R-Ce-Cu-O (with R = Pr or Nd) by Tan et al.[9] and Liang et al.[11] These shifts have been correlated with the onset of superconductivity in these n-type materials. Raveau et al.[16] recently studied the relation between the Cu K-edge characteristic energy[14] (which is one of the several ways of defining the edge energy) and T_c for powdered $(AO)_m M_2 Ca_{n-1} Cu_n O_{2n+2}$ materials with A = Bi,Tl, M = Sr,Ba, and n = 2,3 (including Bi 2:2:1:2). They found that a shift of the characteristic edge energy by 0.5 eV to higher energy corresponded to a decrease of T_c by about 25–30 K. If this relation is applicable to IBi 2:2:1:2 then, the 0.1-eV upward shift due to iodine intercalation should result in a decrease of T_c by about 5–6 K, which is about half of the total 10-K decrease of the T_c. This suggests that (upon I intercalation) the role of the electronic band shift in the decrease of T_c could be as important as that of the weakened interlayer coupling causing by the c axis expansion. It should also be noted that such an upward shift could cause a reduction in the number of charge states near Fermi level E_F. Thus, the $+0.1$-eV shift of the in-plane Cu states upon I intercalation could make an important contribution to the increase of the in-plane resistivity.[2] In the R-Ce-Cu-O n-type superconductor, adding electrons to the Cu sites shifts the in-plane $4p$ and $3d$ bands downwards[9,11] and simultaneously causes the metallization of the in-plane resistivity and the creation of the superconductivity.[17] In IBi 2:2:1:2, the loss of electron charge from Cu sites should cause opposite effects, i.e., shifting the in-plane $4p$ and $3d$ states to higher energy away from E_F and increasing the in-plane resistivity. This view point is consistent with the anisotropic resistivity results from the recent

transport measurements.[2]

The second spectral change noted above (the slight increase of the intensity of feature B in Fig. 2) could be related to the 0.1-Å expansion of the Bi-Sr distance due to the intercalation.[4] This connection could proceed through the Sr-layer oxygen atom which is apical to the Bi on one side and apical to Cu on the other. Namely, the Bi-Sr dilitation could indicate a relative weakening in the Bi-O(apical) bonding thereby enabling a relative strengthening of the Cu-O(apical) bonding on the other side of the O. Such an increased Cu-O(apical) interaction could slightly weaken the electronic charge transfer from the planar oxygen ligands to the Cu $3d$ hole and could be responsible for the slight intensity increase of the $4p_\pi$ related feature B.

C. Bi L_e-edge results

The polarized Bi L_3-edge spectra for Bi 2:2:1:2 is shown in Fig. 4. The broad double peaked features: labeled by $A_\parallel$ and $B_\parallel$ in the E$\parallel c$ spectrum can be assigned as due to the $2p \rightarrow 6d_{t_{2g}}$ (d_{xz} and d_{yz}) and $2p \rightarrow 6d_{e_g}$ (d_{z^2}), respectively; and labeled by $A_\perp$ and $B_\perp$ in the E$\perp c$ spectrum can be assigned as due to the $2p \rightarrow 6d_{t_{2g}}$ (d_{xy}) and $2p \rightarrow 6d_{e_g}$ ($d_{x^2-y^2}$), respectively.[16,18] It is observed that (1) the intensity ratio $I_{A_\parallel}/I_{B_\parallel}$ in the E$\parallel c$ spectrum is larger than $I_{A_\perp}/I_{B_\perp}$ in the E$\perp c$ spectrum; (2) peak $B_\parallel$ shifts away from peak $B_\perp$ by about $+1.6$ eV peak $A_\parallel$ is located almost at the same position as the peak $A_\perp$; and (3) the edge of E$\parallel c$ spectrum is about 0.8 eV below that of the E$\perp c$ spectrum. These observations can be accounted for qualitatively by ligand field theory. Since there is a much shorter Bi-O(apical) distance of ~ 1.89 Å (compared with $\sim 2.71-2.85$ Å for the other five Bi-O distances)[10] in the BiO$_6$ cluster of Bi 2:2:1:2, the BiO$_6$ can be treated as a compressed octahedra. Thus, the $6d_{t_{2g}}$ and $6d_{e_g}$ orbitals are split[19] such that the energy of the $6d_{z^2}$
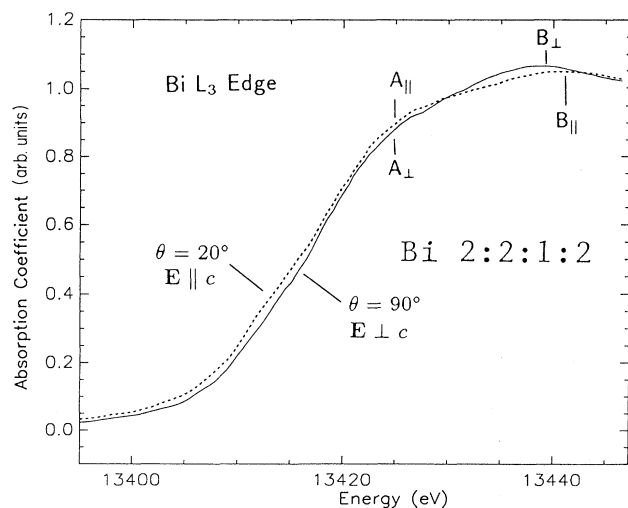
orbital is much higher than that of the $6d_{x^2-y^2}$ orbital but the energy of the degenerate $6d_{xz}$ and $6d_{yz}$ orbitals is just slightly higher than that of the $6d_{xy}$ orbital. Observation (2) above can be accounted for by these splittings. The intensity ratio difference could be attributed to the fact that there are two out-of-plane states d_{xz} and d_{yz} contributing to the feature $A_\parallel$ but only one in-plane state d_{xy} to feature $A_\perp$. Since the feature $A_\parallel$ and $A_\perp$ ride upon the step-shaped continuum onset and the Bi $6d$ states are very broad, the 0.8-eV edge shift could be partially due to the intensity ratio change.

In Fig. 5, we compare the polarized Bi L_3-edge spectra of the IBi 2:2:1:2 and Bi 2:2:1:2 single crystals. The spectrum for Bi metal is taken from Ref. 16 for comparison. It is observed that the iodine intercalation induces simultaneously an about 0.25-eV downward and upward edge shift for the E$\parallel c$-axis and E$\perp c$-axis spectra, respectively. This shift is much larger than the ~ 0.1-eV shift of the Cu K edge. Based on our previous[20] and Retoux et al.'s[16] Bi L_3 edge results for other Bi compounds, a valence change of Bi from $+3$ to $+5$ should correspond to a 2.2–2.5-eV upward shift of the Bi L_3 edge. Thus, 0.25-eV shift of the Bi L_3 edge would corresponding to about 0.2 e^- variation at each Bi site. Compared with about 0.03 e^- loss at each Cu site, this certainly indicate that the effects of the iodine intercalation on electronic structure of the Bi-O layers is much stronger than on the Cu-O layers. This is not surprising since the intercalated iodine layer is adjacent to the Bi-O layers but further away from the Cu-O layers.[1]

We propose the following picture for a qualitative interpretation of the observed anisotropic edge shift. Since the electronegativity of iodine is much smaller than that of oxygen[19] and the Bi-I distance[4] (3.31 Å) in IBi 2:2:1:2
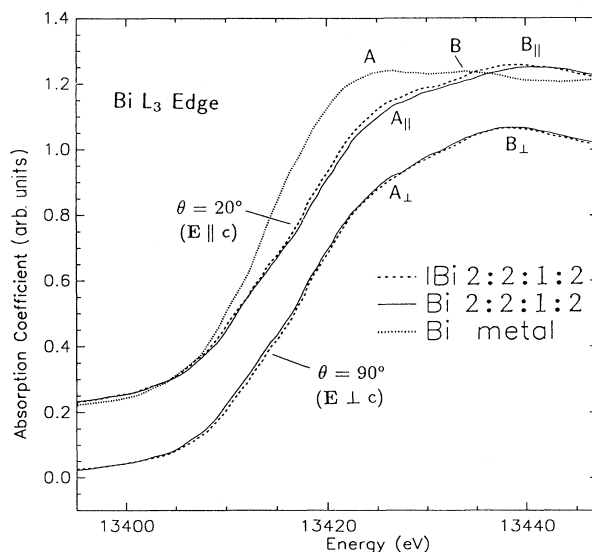

FIG. 4. Polarized Bi L_3 near-edge spectra of single crystal Bi$_2$Sr$_2$CaCu$_2$O$_y$ with E$\perp c$ (solid curve) and E$\parallel c$ (dashed curve).

FIG. 5. Polarized Bi L_3-edge spectra for single crystals Bi$_2$Sr$_2$CaCu$_2$O$_y$ (solid curves) and IBi$_2$Sr$_2$CaCu$_2$O$_y$ (dashed curves) together with data for Bi metal (dotted curve) taken from Ref. 16.
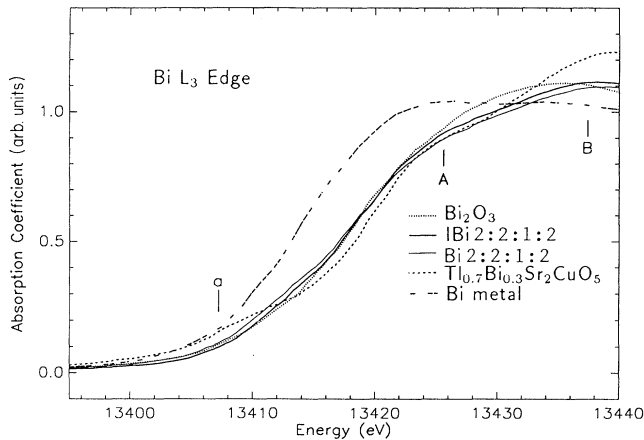
FIG. 6. The Bi L_3 near-edge spectra for powder polycrystalline $IBi_2Sr_2CaCu_2O_y$, $Bi_2Sr_2CaCu_2O_y$, and reference samples.

is much longer than the Bi-O(apical) distance[10] (2.85 Å) in Bi 2:2:1:2, the anion ligands around Bi should become more elongated (or change from octahedral to a pyramidal coordination) upon iodine intercalation. Thus, the ligand field splitting[19] will simultaneously drive the energies of the out-of-plane $6d$ states (d_{xz}, d_{yz}, and d_{z^2}) down and promote the in-plane states (d_{xy}, and $d_{x^2-y^2}$) upward. This would result in an anisotropic edge shift (as observed) because of the broad nature of the $6d$ bands. Note that for the same reason discussed previously, the d_{z^2} should be affected the most. Indeed, we observe in Fig. 5 a clear shift of about -2 eV for the feature $B_\parallel$ but little visible shift for the feature $A_\parallel$ upon intercalation.

It is interesting to note that the edge shift brings the $E\|c$ L_3 edge of IBi 2:2:1:2 closer to the L_3 spectrum of metallic Bi (relative to the unintercalated material). Detailed analysis shows that, upon intercalation, the intensities and energy positions of the $A_\parallel$ and $B_\parallel$ features evolve in a similar manner towards those of the A and B features for Bi metal. This observation suggests that the iodine intercalation might have created a more metalliclike environment for the Bi along the c-axis direction, and is fully consistent with the important finding[2] that the normal-state out-of-plane resistivity changes from the semiconductinglike in Bi 2:2:1:2 to metalliclike in IBi 2:2:1:2. The behavior of the in-plane resistivity, which increases upon intercalation,[2] is also supported by our in-plane $E\|c$ Bi L_3 spectra, i.e., shift away from metallic

Bi is observed. However, we caution that the increase of the in-plane resistivity should be dominated by the in-plane electronic state change of the Cu-O layer (as discussed previously) rather than the Bi-O layer.

In Fig. 6, we show the L_3 edges of powdered samples of IBi 2:2:1:2, Bi 2:2:1:2, along with those of several reference samples. The shape of the IBi 2:2:1:2 spectrum relative to that of the Bi 2:2:1:2 is consistent with the combination of the in-plane and out-of-plane spectra in Fig. 5. Feature A and B are due to $2p \rightarrow 6d_{t_{2g}}$ and $2p \rightarrow 6d_{e_g}$ transitions, respectively. The pre-edge feature a, which has been assigned to the $2p \rightarrow 6s$ transition,[16,18,20] is an indication of the presence of the Bi^{+5} state. Feature a is prominent for Bi^{3+}/Bi^{5+} mixed material $Tl_{0.7}Bi_{0.3}Sr_2CuO_5$,[20] but it is absent for Bi_2O_3 and both the powder and crystal IBi 2:2:1:2 and Bi 2:2:1:2 samples. Thus, Bi in both Bi 2:2:1:2 and IBi 2:2:1:2 has the same filled $6s^2$ configuration as that of Bi_2O_3. The edge energy for IBi 2:2:1:2, defined as the midpoint energy of the main step, is slightly higher than that for Bi 2:2:1:2. This suggests that only a small fraction of electronic charge could have been transferred from Bi-O layers to the iodine layers.

IV. CONCLUSION

In summary, our polarized x-ray absorption spectroscopy results indicate that the intercalated I layers extract electronic charge from the adjacent Bi-O layers and other layers. The I $5p$ orbital hole states in the single crystal IBi 2:2:1:2 are predominantly in-plane states. Even though the iodine intercalation has very small effects on the Cu valence and the electronic structure of the CuO_2 layers, these effects could nevertheless be contributing factors in the 10-K decrease of T_c. The in-plane and out-of-plane Bi $6d$ states are shifted due to a change of the Bi-O ligand coordination from octahedral to pyramidal, possibly resulting in a more metalliclike environment along the c axis for the Bi sites. Our results suggest that a small fraction of electronic charges may have been transferred from Bi-O and Cu-O layers to the iodine layers upon intercalation.

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