In situ temperature-dependent x-ray-absorption spectroscopic studies for the mercury-based superconductors

Seong-Ju Hwang and Jin-Ho Choy*

Department of Chemistry, Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea

Nam Hwi Hur

Superconductivity Laboratory, Korea Research Institute of Standards and Sciences, Taejon 305-600, Korea

(Received 23 April 1997)

In situ temperature-dependent x-ray-absorption spectroscopic studies have been carried out for the mercurybased cuprate superconductor $Hg_{0.5}TI_{0.5}Ba_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$ in order to examine the evolution of electronic and geometric structures below and above the superconducting transition temperature ($T_c = 128$ K). According to the *in situ* Cu *K*-edge x-ray-absorption near-edge structure (XANES) analyses, it is found that the copper valence is remarkably enhanced with a partial formation of Cu(III) ions in the superconducting state, reflecting a lattice instability around copper upon the superconducting transition, which is also confirmed by the *in situ* Hg L_{III^-} and Tl L_{III} -edge XANES analyses. Such a finding underlines that the phonon-mediated pairing mechanism makes a significant contribution to the superconductivity of the Hg-based cuprates. On the other hand, the systematic Cu *K*-edge XANES spectroscopic studies for a series of $Hg_{1-x}Tl_xBa_2(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2n+2+\delta}$ (x=0 and 0.5; n=1, 2, and 3) superconductors have also been performed, which allows us to determine the effects of the Tl substitution and the number of (Cu-O) sheet per formula unit (n) on the hole concentration of the copper-oxygen layer. [S0163-1829(98)09701-X]

I. INTRODUCTION

After the observation of the highest superconducting transition temperature (T_c) of 134 K in mercury-based copper oxides, HgBa₂Ca_{n-1}Cu_nO_{2n+2+ δ} (n=1, 2, and 3), intense research has been performed to understand the superconducting property and mechanism for these materials.^{1,2} Moreover, T_c of ca. 160 K was reported for HgBa₂Ca₂Cu₃O_{8+ δ} (Hg-1223) under pressure,^{3,4} which induces many research efforts to reproduce such a high transition temperature under an ambient atmosphere by applying chemical pressure through cation substitution.^{5,6} However, only a few spectroscopic studies on their electronic structures were performed to elucidate the origin of remarkable T_c increase under pressure.^{7,8} In particular, a comparative study in normal and superconducting states has not been carried out so far, even though it can provide direct and valuable information on superconducting mechanisms in these compounds. This might be due to the difficulty in obtaining the homogeneous sample and/or due to its instability. Recently we found that the Tl ion in the (Hg-O) rock salt layer by a partial substitution of Hg gives rise to a stabilization of the Hg-1223 phase as well as to an enhancement of critical current density.⁶ More interestingly, the Tl substituted $Hg_{0.5}Tl_{0.5}Ba_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$ (Hg, Tl-1223) compound shows an increase of T_c after Ar annealing,⁶ suggestive of a hole overdoped state, in contrast to the unsubstituted case.⁹ Therefore, it is thought to be an interesting example for studying the mechanism of internal charge transfer for the Hg-based cuprates. In this respect, Hg, Tl-1223 is expected to be quite suitable for the temperature-dependent experiment.

Previously we have performed the systematic Cu K-edge

x-ray-absorption spectroscopic (XAS) study for the chemically well-defined divalent and trivalent copper oxides, which allows us to identify clearly all the fine features in the Cu K-edge x-ray-absorption near-edge structure (XANES) region.¹⁰ On the basis of this assignment, we have successfully applied XANES analysis in examining the electronic structure of various high- T_c superconducting systems including the superconducting intercalation compounds.11-15 Now we are going to extend our XANES studies to the Hg-based cuprates, since it can provide a sensitive probe for a change in local structure as well as for a modification of electronic configuration in these compounds. A more remarkable advantage is that it easily provides the bulk properties indispensable for clarifying the electronic structures of these compounds, in contrast to the other surface sensitive method such as x-ray photoelectron spectroscopy.⁷

In this work, we have thoroughly carried out the *in situ* temperature-dependent XAS studies at the Cu *K*, Hg L_{III} , and Tl L_{III} edges for the Tl substituted Hg-1223 phase Hg_{0.5}Tl_{0.5}Ba₂(Ca_{0.86}Sr_{0.14})₂Cu₃O_{8+ δ} in order to probe the evolution of electronic and crystal structures before and after the superconducting transition as well as to examine the role of the charge reservoir layer. In addition, the effect of Tl substitution and the number of (Cu-O) layers per formula unit on the electronic structure of the copper-oxygen layer has also been investigated by performing the Cu *K*-edge XANES analyses for the Hg_{1-x}Tl_xBa₂(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2n+2+ δ} (*x*=0 and 0.5; *n* = 1, 2, and 3) compounds.

II. EXPERIMENT

The polycrystalline samples of $Hg_{1-x}Tl_xBa_2(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2n+2+\delta}$ (x=0.0 and 0.5;

<u>57</u>

1259

© 1998 The American Physical Society

TABLE I. Lattice parameters and superconducting transition temperatures $(T_c$'s) of the $Hg_{1-x}Tl_xBa_2(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2n+2+\delta}$ (x=0 and 0.5; n=1, 2, and 3) compounds.

Compounds	a (Å) ^a	c (Å) ^a		T_c (K)	
$HgBa_2CuO_{4+\delta}$	3.8868(2)	9.4886(1)	92 ^b		
HgBa ₂ Ca _{0.86} Sr _{0.14} Cu ₂ O _{6+δ}	3.8584(1)	12.6646(5)	120 ^b	124 ^c	
$Hg_{0.5}Tl_{0.5}Ba_2(Ca_{0.86}Sr_{0.14})Cu_2O_{6+\delta}$	3.8496(1)	12.6536(4)	122 ^b	100 ^c	122 ^d
$HgBa_{2}(Ca_{0.86}Sr_{0.14})_{2}Cu_{3}O_{8+\delta}$	3.8648(2)	16.0319(2)	126 ^b	132 ^c	
$Hg_{0.5}Tl_{0.5}Ba_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{\delta^+\delta}$	3.8649(1)	15.9573(2)	128 ^b	120 ^c	132 ^d

^aX-ray-diffraction peaks could be well indexed on the basis of a tetragonal unit cell with a space group of P4/mmm.

^bThe sample as-sintered.

°The sample annealed under oxygen atmosphere ($P_{O2}=1$ atm) at 250 °C for 8 h (Hg-1212), 350 °C for 8 h (Hg, Tl-1212), 280 °C for 10 h (Hg-1223), and 400 °C for 6 h (Hg, Tl-1223).

^dThe sample annealed under argon atmosphere (P_{Ar} =1 atm) at 350 °C for 8 h (Hg, Tl-1212) and 400 °C for 6 h (Hg, Tl-1223).

n=1, 2, and 3) were prepared from stoichiometric amounts of HgO, Tl_2O_3 , and ternary oxides Ba_2CuO_{3+x} and $Ca_{0.86}Sr_{0.14}CuO_2$, as described previously.^{6,9,16,17} The crystal structure of the present compounds was determined by powder x-ray-diffraction analysis with a Rigaku automatic diffractometer equipped with a Cu $K\alpha$ radiation. In order to check out whether the as-sintered samples are in a hole underdoped state or in a hole overdoped one, the effects of Ar and O₂ annealings on their superconducting properties were examined using a superconducting quantum interference device magnetometer with an applied field of 20 G. The obtained superconducting transition temperatures (T_c) are summarized in Table I together with the lattice parameters determined by Rietveld analysis. For the Tl substituents, the complete substitution of thallium for mercury site was confirmed by performing the thermogravimetric analysis and electron probe microanalysis.

The present x-ray-absorption spectra were measured with synchrotron radiation by using extended x-ray-absorption fine structure facilities installed at the beam line 10B at the Photon Factory in Tsukuba, operated at 2.5 GeV and 260 $\sim\!370~\text{mA}.^{18}$ The samples were finely ground, mixed with boron nitride in an appropriate ratio, and pressed into pellets in order to obtain an optimum absorption jump $(\Delta \mu t \approx 1)$ enough to be free from the thickness and pinhole effects.¹⁹ For in situ experiments, the samples were mounted in a metal holder attached to the cold finger of a liquid He cryostat. All the present spectra were obtained in a transmission mode using gas-ionization detectors. To ensure the spectral reliability, much care was taken to evaluate the stability of the energy scale by monitoring the spectra of Cu metal, HgO, and Tl_2O_3 for each measurement, and thus edge positions were reproducible to better than 0.05 eV. The inherent background in the data was removed by fitting a polynomial to the pre-edge region and extrapolated through the entire spectrum, from which it was subtracted. The resulting spectra, $\mu(E)$, were normalized to an edge jump of unity for comparing the XANES features directly with one another.

III. RESULTS AND DISCUSSION

Figure 1(a) represents the Cu *K*-edge XANES spectra for the HgBa₂(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2 $n+2+\delta$} (n=1, 2, and 3) compounds, together with those for the references of Nd_2CuO_4 , La_2CuO_4 , $LaCuO_3$, and $La_2Li_{0.5}Cu_{0.5}O_4$, where a divalent or trivalent copper ion is stabilized with different local geometries. It is found that the edge energies of Hg-based cuprates are lower than those of Cu(III) references but higher than those of Cu(II) ones, indicating the mixed-valence state of copper [Cu(II)/Cu(III)]. Among the super-conducting compounds, there is an overall spectral shift to-ward lower energy side with increasing the number of the (Cu-O) layer per unit formula (n), even though the band calculation predicted that the self-doping mechanism be-



FIG. 1. Cu *K*-edge XANES (a) spline and (b) second derivative spectra for HgBa₂(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2 $n+2+\delta$} with (i) n=1, (ii) 2, and (iii) 3, (iv) Nd₂CuO₄, (v) La₂CuO₄, (vi) LaCuO₃, and (vii) La₂Li_{0.5}Cu_{0.5}O₄, respectively.

comes more efficient with increasing $n.^{20}$ Therefore, it is suggested that the doped hole in the Hg-based cuprates is mainly originated from the excess oxygen in the (Hg-O) plane rather than from the internal charge transfer process.

In order to identify all the fine spectral features, each spectrum has been carefully analyzed by using the second differential method that is quite effective in differentiating a small difference of spectral features [Fig. 1(b)].²¹ A small pre-edge peak (denoted as P) is observed commonly for all the present compounds, which is assigned to the transition from the core 1s level to the unoccupied 3d state. Even though it is not allowed by the electronic dipolar selection rule $\Delta l = \pm 1$, the pre-edge peak A can be observed either due to a quadrupole transition and/or due to a mixing of 4pand 3d states.²² The energy of this peak for the Hg-based cuprates is found to be slightly higher than those for Cu(II) references but surely lower than those for Cu(III) ones, confirming again the mixed-valence state of copper [Cu(II)/ Cu(III) in these compounds. In the main edge region, there are some peaks corresponding to the dipole-allowed transitions from the core 1s level to the unoccupied 4p states, which are denoted as A, B, and C, as observed for other superconducting copper oxides.^{11–13} According to our previous Cu K-edge XAS study,¹⁰ the main edge features A and B are attributed to the transition from the 1s orbital to the out-of-plane $4p_{\pi}$ one with and without shakedown processes, respectively, whereas the feature C is ascribed to the in-plane $4p_{\sigma}$ final-state transition without shakedown process. Among them, peak A has been known to reflect sensitively a modification of the local structure around the copper ion.¹⁰ For the sake of a clear understanding of the relationship between the spectral feature of this peak and the local structure of copper, the crystal structures of all the present copper oxides are illustrated in Fig. 2. It is clearly observed from Fig. 1(b) that peak A is less intense with a higher transition energy for La₂CuO₄ compared to Nd₂CuO₄. Because the copper ion is stabilized in the tetragonally distorted octahedral symmetry for the former but in the square planar one for the latter, the observed spectral differences for both compounds can be well explained from the fact that the shakedown process by the ligand-to-metal charge transfer (LMCT) is effectively reduced by the presence of axial oxygens through the electrostatic repulsion. For the case of Hgbased cuprates, there is a decreasing trend in the energy of peak A with increasing the number of the (Cu-O) layer per unit cell (n), which can be also explained successfully from the viewpoint of crystal structure;²³ as the local symmetry of copper is changed from octahedral to square pyramidal (or to square planar), LMCT along the c axis becomes electrostatically favorable, resulting in a downward shift of this shakedown peak. Such an interpretation is supported from the fact that the peak position for the n = 1 phase is very close to that for La₂CuO₄ with the same local symmetry of copper. In contrast to the shakedown process through the π -bonding channel, the LMCT process along the σ bonding is too difficult to occur for the divalent copper compound due to a large electrostatic repulsion created by four equatorial oxygens. But, in the case of $La_2Li_{0.5}Cu_{0.5}O_4$, where the trivalent copper ion is stabilized in an anisotropic crystal field, the shakedown peaks A and A' are commonly observed, those that correspond to the transitions to the $|1s^{1}3d^{9}4p_{\pi}^{1}L^{-1}\rangle$



FIG. 2. Schematic representation of the crystal structure for HgBa₂(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2 $n+2+\delta$} with (a) n=1, (b) 2, and (c) 3, and for the references of (d) Nd₂CuO₄, (e) La₂CuO₄ (or La₂Li_{0.5}Cu_{0.5}O₄), and (f) LaCuO₃. Note that the oxygen site on the Hg layer of the Hg-based cuprates is partially occupied.

final state and to the $|1s^{1}3d^{9}4p_{\sigma}^{1}L^{-1}\rangle$ one, respectively, through both π - and σ -bonding channels. This indicates that the increase of the copper valence makes the shakedown process to the $4p_{\sigma}$ orbital energetically favorable through the electrostatically enhanced attractive potential of trivalent copper, in contrast to the divalent copper compounds.²⁴ In this respect, the peak A' provides an evidence for the presence of the Cu(III) ion, as confirmed by XANES study for the chemically and electrochemically prepared $La_2CuO_{4.08}$.¹¹ In contrast to the hole overdoped Bi-based cuprates,¹³ the peak A' cannot be observed for all the present Hg-based cuprates, indicating that they are hole deficient as expected from the fact that their T_c 's are significantly increased by annealing in oxygen atmosphere and by applying high pressure.^{3,4,9} This is also supported by the previous thermoelectric power measurements clarifying the underdoped hole concentration of the as-sintered samples of HgBa₂Ca_{n-1}Cu_nO_{2 $n+2+\delta$} (n=1, 2, and 3).²⁵

On the basis of the present peak assignment, we have investigated the effect of Tl substitution on the electronic and geometric structures of the CuO₂ layer. The Cu *K*-edge XANES spline and second derivative spectra for the $Hg_{1-x}Tl_xBa_2(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2n+2+\delta}$ (x=0 and 0.5; n= 2 and 3) compounds are represented in Figs. 3(a) and 3(b), respectively. The most striking spectral change upon Tl substitution is a remarkable broadening of peak *A*, indicating the presence of two different copper sites with an axial oxygen coordinated to the Tl(III) ion or to the Hg(II) one. Taking into account the higher oxidation state of the Tl(III) ion compared to the Hg(II) one, the [Tl(III)-O] bond is expected to



be stronger than the [(Hg(II)-O)] one, therefore, the competing [Cu-O_{axial}] bond is weaker for the (Tl-O-Cu) pair with respect to the (Hg-O-Cu) one. As a result, the LMCT process between Cu and O_{axial} becomes easier for the former pair due to a decrease of repulsive force between the Cu $4p_{\pi}$ electron and oxygen ligand, which gives rise to a shoulder peak at the lower energy side of peak A upon Tl substitution.

In contrast to the peak broadening, there is no distinct difference in the edge position between the Tl-substituted compound and the unsubstituted one, indicating that Tl substitution does not induce any significant change in the hole concentration of the CuO₂ layer. As listed in Table I, T_c of Hg, Tl-1223 is found to increase after heat treatment under argon atmosphere ($P_{Ar}=1$ atm) in contrast to the Hg-1223 case,^{6,9} suggesting that the hole underdoped state of the Hg-1223 phase is changed to the hole overdoped one by substituting Hg(II) with Tl(III). But, the present XANES results rule out the possibility of a change in hole concentration upon Tl substitution. Therefore, the different T_c variation between Hg-1223 and Hg, Tl-1223 after Ar annealing should be attributed to the modification of the charge reservoir layer. According to the recent band calculation on the oxygenated Hg-1223 phase,²⁶ it was found that the internal charge transfer between the charge reservoir (Hg-O) layer and the superconductive (Cu-O) one is reduced effectively by an increase of oxygen content. Since the substitution of the Tl(III) ion for the Hg(II) one increases the amount of excess oxygen, 2^7 it is expected that the role of the charge



FIG. 4. Cu *K*-edge XANES (a) spline and (b) second derivative spectra for $Hg_{0.5}Tl_{0.5}Ba_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$ at (i) 300 K and (ii) 34 K, (iii) La₂CuO₄, and (iv) La₂Li_{0.5}Cu_{0.5}O₄, respectively.

reservoir layer is depressed for the Hg, Tl-1223 phase compared to the Hg-1223 one. On the basis of this expectation, it is suggested that Ar annealing for Hg, Tl-1223 gives rise to a slight oxygen loss, resulting in an improvement of the selfdoping mechanism.²⁸ As a result, the hole concentration in the CuO₂ layer increases with an increase of T_c .

Figures 4(a) and 4(b) represent the temperature-dependent Cu K-edge XANES spectra and their second derivatives for Hg, Tl-1223 in superconducting (34 K) and normal states (300 K), respectively, together with those for La_2CuO_4 and $La_2Li_{0.5}Cu_{0.5}O_4$. It is obvious that peaks A, B, and C commonly shift to a higher energy side in the superconducting state compared to the normal one, suggesting an enhancement of copper valence below T_c . In addition to the overall peak shift, we can observe a remarkable difference in the Cu K-edge XANES spectra; an appearance of an additional shoulder (A') at 8986 eV for the low-temperature spectra. This difference can be more clearly seen in the corresponding second derivatives as shown in Fig. 4(b). As described above, such a peak is attributed to the $1s \rightarrow 4p_{\sigma}$ transition accompanied by a shakedown process through the LMCT process and is characteristic of trivalent copper. In this respect, the occurrence of peak A' provides an explicit evidence of partial formation of Cu(III) in the superconducting state, which is well consistent with an increase of copper valence. Since the oxidation state of copper is closely related to the bond distance of (Cu-O), the high-energy shift of peaks A, B, and C corresponding to the transitions to the antibonding Cu $4p_{\pi}$ and $4p_{\sigma}$ states can be interpreted as a result of the contraction of in-plane and out-of-plane (Cu-O)



FIG. 5. Hg $L_{\rm III}$ -edge XANES (a) spline and (b) second derivative spectra for Hg_{0.5}Tl_{0.5}Ba₂(Ca_{0.86}Sr_{0.14})₂Cu₃O_{8+ δ} at (i) 300 K and (ii) 34 K, and for the references of (iii) HgO, (iv) HgBr₂, and (v) HgI₂, respectively. The inset in (b) provides an expanded view of second derivative spectra for HgO (dotted line) and Hg_{0.5}Tl_{0.5}Ba₂(Ca_{0.86}Sr_{0.14})₂Cu₃O_{8+ δ} in the superconducting state (solid line) and the normal one (dashed line) with an energy range of 12 278–12 287 eV.

bonds in the superconducting state, leading to the destabilization of antibonding Cu 4p orbitals. Therefore, the present results demonstrate clearly that there is a remarkable change in the local structure of the (Cu-O) layer before and after superconducting transition. Although the lattice instability in the superconducting state has been observed for various high- T_c oxides by other sensitive methods, $^{29-32}$ such a remarkable change in the present Cu K-edge XANES spectra has so far never been observed for any other superconducting materials. It is, therefore, concluded that the phononmediated interaction contributes more significantly to the superconductivity of the Hg-based cuprates, compared to the other high- T_c superconducting oxides. Such a conclusion is also supported from an extreme T_c enhancement of the Hgbased cuprates under high pressure.^{3,4} Moreover, the previous in situ neutron-diffraction study revealed that the axial (Cu-O) bond of Hg-based cuprates has an extreme compressibility under high pressure, implying that this bond is closely related with the T_c enhancement under high pressure.³³

The *in situ* Hg L_{III} and Tl L_{III} -edge XANES analyses were also made to investigate the electronic and geometric structures of the charge reservoir layer in normal and superconducting states. Figures 5(a) and 5(b) represent the Hg L_{III} -edge XANES spline spectra and their second derivatives for Hg, Tl-1223 in the superconducting state (34 K) and the normal one (300 K), respectively, together with those for the HgO, HgBr₂, and HgI₂ references. As predicted by the dipolar selection rule, not only the main-edge peaks B and C corresponding to $2p_{3/2} \rightarrow 6d$ transitions, but also the pre-edge peak A corresponding to the $2p_{3/2} \rightarrow 6s$ one is observed commonly for all the present compounds, because they contain a Hg(II) ion with vacant 6s and 6d orbitals.^{8,34} Among these spectral features, the pre-edge peak A can provide a sensitive probe to the bonding environment of the mercury ion. Actually, this peak is less prominent for the references HgX_2 (X =Br and I) compared to the Hg-based cuprates and HgO, which is surely attributed to the stronger covalency of mercury-halogen bond rather than mercury-oxygen one. It is also found that the intensity of peak A is stronger for Hg-1223 than for HgO, which can be understood by considering the (Hg-O) bond covalency that is larger for the latter with four extra oxygens present in the plane perpendicular to the dumbbell axis in HgO. Such an enhanced covalency gives rise to a partial electron transfer to the Hg 6s level, and consequently to a decrease of hole density in the final Hg 6s state, with respect to the Hg-based cuprate with significant oxygen vacancies in the (Hg-O) layer.²⁷ Comparing the position of the edge jump, the oxidation state of the mercury ion in the Hg-1223 phase is estimated to be nearly the same with the divalent state or slightly higher than that. But taking into account the fact that the Hg(III) ion can be formed only by removing one electron from the completely filled 5d orbital, which needs an unusually large energy expense, a remarkable increase of edge position is expected for the trivalent mercury ion compared to the divalent one. In this respect, the small energy difference between the Hg-based cuprate and HgO indicates that the amount of the Hg(III) ion is, if any, negligible for the Hg, Tl-1223 phase.

A closer comparison of the Hg L_{III} -edge second derivative spectra in superconducting and normal states reveals a slight enhancement of peak A below T_c , implying a decrease of the (Hg-O) bond covalency. Since the amount of excess oxygen in the (Hg-O) layer remains unchanged before and after the superconducting transition, an increase of the peak intensity is ascribed to an elongation of the (Hg-Oaxial) bond. From the viewpoint of the crystal structure where the axial oxygen is coordinated to the copper ion in the one direction and to the mercury ion in the other one,²⁷ an increase of the (Hg-Oaxial) bond distance indicates a contraction of the competing (Cu-Oaxial) bond, which coincides with the present Cu K-edge XANES results. A weakening of the (Hg-O_{axial}) bond after the superconducting transition has been already pointed out from the in situ Raman study where the Raman peak corresponding to the axial oxygen motion is softened below T_c .³⁵

Figures 6(a) and 6(b) represent the Tl L_{III} -edge XANES spectra and their second derivatives for Hg, Tl-1223 in the superconducting state (34 K) and the normal one (300 K), respectively, together with that for the reference Tl₂O₃. Like the Hg L_{III} edge, there are three broad peaks, indicated as *A*, *B*, and *C*, in the Tl L_{III} -edge spectra, which correspond to the transitions to 6*s* and 6*d* final states.³⁶ As can be seen clearly from Fig. 6(b), peak *A* is found to be more intense for Hg, Tl-1223 than for Tl₂O₃, which can be well understood as a result of the different occupation of the 6*s* orbital by the adjacent (Tl-O) bonds.³⁷ From the edge position, the oxida-



FIG. 6. Tl $L_{\rm III}$ -edge XANES (a) spline and (b) second derivative spectra for Hg_{0.5}Tl_{0.5}Ba₂(Ca_{0.86}Sr_{0.14})₂Cu₃O_{8+ δ} at (i) 300 K and (ii) 34 K, and for (iii) the reference Tl₂O₃. The inset in (b) provides an expanded view of second derivative spectra for Tl₂O₃ (dotted line) and Hg_{0.5}Tl_{0.5}Ba₂(Ca_{0.86}Sr_{0.14})₂Cu₃O_{8+ δ} in the superconducting state (solid line) and the normal one (dashed line) with an energy range of 12 648–12 657 eV.

tion state of thallium in Hg, Tl-1223 is determined to be trivalent as observed in the TlBa₂Ca₂Cu₃O_{8+ δ} phase.³⁶ Like the Hg $L_{\rm III}$ edge, the intensity of the pre-edge peak *A* is observed to be stronger for the low-temperature spectrum compared to the high-temperature one, reflecting again the structural deformation around copper. Summarizing the present Hg $L_{\rm III}$ - and Tl $L_{\rm III}$ -edge XANES results, the internal charge transfer between the (Hg, Tl-O) layer and the (Cu-O)

*To whom all correspondence should be addressed. Fax: (82) 2-872-9864; Tel: (82) 2-880-6658; Electronic address: jhchoy@plaza.snu.ac.kr

- ¹S. N. Putlin, E. V. Antipov, O. Chmaissem, and M. Marezio, Nature (London) **362**, 226 (1993).
- ²A. Schilling, M. Cantoni, J. D. Gao, and H. R. Ott, Nature (London) **363**, 56 (1993).
- ³C. W. Chu, L. Gao, F. Chen, Z. J. Huang, R. L. Meng, and Y. Y. Xue, Nature (London) **365**, 323 (1993).
- ⁴L. Gao, Y. Y. Xue, Y. Cao, F. Chen, Y. Y. Sun, J. Gibson, C. W. Chu, L. M. Liu, and A. Jacobson, Phys. Rev. B **50**, 10 346 (1994).
- ⁵K. Isawa, A. Tokiwa-Yamamoto, M. Itoh, S. Adachi, and H. Yamauchi, Physica C **217**, 11 (1993); O. Chmaissem, J. D. Jorgensen, K. Yamaura, Z. Hiroi, M. Takano, J. Shimoyama, and K. Kishio, Phys. Rev. B **53**, 14 647 (1996); Z. H. He, Q. M. Lin,

one is not effective in the present Hg, Tl-1223 compound and there is a slight local distortion of the charge reservoir layer in the superconducting state, which might reflect the lattice deformation around the copper ion.

IV. CONCLUSION

In this work, we have investigated the evolution of electronic and crystal structures upon the superconducting transition by performing in situ temperature-dependent XANES analyses for $Hg_{0.5}Tl_{0.5}Ba_2(Ca_{0.86}Sr_{0.14})_2Cu_3O_{8+\delta}$ From these studies, it is found that the copper valence is enhanced with a partial formation of Cu(III) species in the superconducting state, reflecting a lattice instability around the copper ion below T_c . Such a result provides clear evidence of a significant electron-phonon interaction in the Hg-based cuprates, which can be interpreted as the origin of the previously reported extreme T_c enhancement under high pressure. Taking into account the fact that such a remarkable change in the present Cu K-edge XANES spectra has never been observed for any other superconducting materials, it is concluded that the phonon-mediated interaction contributes more significantly to high- T_c superconductivity of Hg-based cuprates. On the other hand, the systematic Cu K-edge XANES results for $Hg_{1-x}Tl_xBa_2(Ca_{0.86}Sr_{0.14})_{n-1}Cu_nO_{2n+2+\delta}$ (x = 0 and 0.5; n=1, 2, and 3 indicate that the average oxidation state of the (Cu-O) layer is decreased with an increase of n whereas it is not significantly changed by Tl substitution. On the basis of these findings, it is claimed that the doped hole in the Hg-based cuprates is mainly originated from the excess oxygen in the (Hg-O) plane rather than from the internal charge transfer and that the different T_c variation of Hg-1223 and Hg, Tl-1223 after Ar annealing is due to the modification of the charge reservoir layer.

ACKNOWLEDGMENTS

This work was in part supported by the Ministry of Science and Technology for the high-temperature superconductivity research and by the Korea Science and Engineering Foundation through the Center for Molecular Catalysis. The authors are grateful to Professor M. Nomura for helping us to get the XAS data at the Photon Factory.

L. Gao, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Physica C **241**, 211 (1995); C. Michel, M. Hervieu, A. Maignan, D. Pelloquin, V. Badri, and B. Raveau, Physica C **241**, 1 (1995).

- ⁶N. H. Hur, N. H. Kim, K. W. Lee, Y. K. Park, and J. C. Park, Mater. Res. Bull. **29**, 959 (1994); N. H. Hur, N. H. Kim, K. W. Lee, K. H. Yoo, Y. K. Park, and J. C. Park, Physica C **234**, 19 (1994).
- ⁷H.-D. Kim, S.-J. Oh, I.-S. Yang, and N. H. Hur, Physica C 253, 351 (1995); R. P. Vasquez, M. Rupp, A. Gupta, and C. C. Tsuei, Phys. Rev. B 51, 15 657 (1995); C. S. Gopinath, N. H. Hur, and S. Subramanian, *ibid.* 52, R9879 (1995).
- ⁸F. Studer, D. Pelloquin, A. Maignan, C. Michel, H. Hervieu, and B. Raveau, Physica C **242**, 1 (1995); E. Pellegrin, J. Fink, C. T. Chen, Q. Xiong, Q. M. Lin, and C. W. Chu, Phys. Rev. B **53**, 2767 (1996).
- ⁹N. H. Hur, N. H. Kim, Y. K. Park, and J. C. Park, J. Mater. Res.

10, 2985 (1995); R.-L. Meng, L. Beauvais, X. N. Zhang, Z. Y. Huang, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Physica C **216**, 21 (1993).

- ¹⁰J.-H. Choy, D.-K. Kim, S.-H. Hwang, and G. Demazeau, Phys. Rev. B **50**, 16 631 (1994).
- ¹¹J.-H. Choy, D.-K. Kim, S.-H. Hwang, and J.-C. Park, J. Am. Chem. Soc. **117**, 7556 (1995).
- ¹² J.-H. Choy, D.-K. Kim, S.-G. Kang, D.-H. Kim, and S.-J. Hwang, in *Superconducting Materials*, edited by J. Etourneau, J.-B. Torrance, and H. Yamauchi (IITT-International, Paris, 1993), p. 329.
- ¹³J.-H. Choy, S.-J. Hwang, and N.-G. Park, J. Am. Chem. Soc. **119**, 1624 (1997).
- ¹⁴J.-H. Choy, N.-G. Park, S.-J. Hwang, and Z.-G. Khim, J. Phys. Chem. **100**, 3783 (1996).
- ¹⁵J.-H. Choy, D.-K. Kim, N.-G. Park, D.-H. Kim, S.-J. Hwang, S.-H. Hwang, and N. H. Hur, Physica C 235-240, 1023 (1994).
- ¹⁶N. H. Hur, N. H. Kim, S. H. Kim, Y. K. Park, and J. C. Park, Physica C **231**, 227 (1994); N. H. Hur, N. H. Kim, K. W. Lee, Y. K. Park, and J. C. Park, *ibid.* **231**, 4 (1994).
- ¹⁷N. H. Hur, I. S. Kim, Y. K. Park, and J. C. Park, Bull. Korean Chem. Soc. **15**, 3 (1994).
- ¹⁸H. Oyanagi, T. Matsushida, M. Ito, and H. Kuroda, KEK Report No. 83, 1984 (unpublished); H. Kuroda and A. Koyama, KEK Report No. 84, 1989 (unpublished).
- ¹⁹F. W. Lytle, G. van der Laan, R. B. Greegor, E. M. Larson, C. E. Violet, and J. Wong, Phys. Rev. B **41**, 8955 (1990); E.-A. Stern and K. Kim, *ibid.* **23**, 3781 (1981).
- ²⁰D. J. Singh, Phys. Rev. B 48, 3571 (1993).
- ²¹F. W. Lytle and R. B. Greegor, Appl. Phys. Lett. 56, 192 (1990).
- ²²J. E. Hahn, R. A. Scott, K. O. Hodgson, S. Doniach, S. R. Desjardins, and E. I. Solomon, Chem. Phys. Lett. 88, 595 (1982).
- ²³As shown in Fig. 2, the copper ion is stabilized in the tetragonally distorted CuO₆ octahedron for the n=1 phase and in the CuO₅ square pyramid for the n=2 one whereas a unit cell of the n=3 phase contains two copper ions in the CuO₅ square pyramid and one in the square planar symmetry.
- ²⁴Because the copper 4p orbitals are isotropic in LaCuO₃ with a regular CuO₆ octahedron, there is no splitting of peaks A and A' for this compound.

- ²⁵C. K. Subramaniam, M. Paranthaman, and A. B. Kaiser, Physica C 222, 47 (1994); Y. T. Ren, J. Clayhold, F. Chen, Z. J. Huang, X. D. Qiu, Y. Y. Sun, R. L. Meng, Y. Y. Xue, and C. W. Chu, *ibid.* 217, 6 (1993); C. K. Subramaniam, M. Paranthaman, and A. B. Kaiser, Phys. Rev. B 51, 1330 (1995).
- ²⁶D. J. Singh and W. E. Pickett, Phys. Rev. Lett. 73, 476 (1994).
- ²⁷P. Dai, B. C. Chakoumakos, G. F. Sun, K. W. Wong, Y. Xin, and D. F. Lu, Physica C **243**, 201 (1995).
- ²⁸ Although the oxygen loss during Ar annealing would give rise to a decrease of hole concentration of the CuO₂ layer, the recent band calculation in Ref. 26 showed that an increase of hole density induced by excess oxygen is considerably lower than that expected from formal ionic consideration. Therefore, the T_c enhancement after Ar annealing indicates that the improvement of internal charge transfer prevails over a small decrease of hole density due to the oxygen loss.
- ²⁹S. Conradson, I. D. Raistrick, and A. R. Bishop, Science 248, 1394 (1990).
- ³⁰B. H. Toby, T. Egami, J. D. Jorgensen, and M. A. Subramaniam, Phys. Rev. Lett. **64**, 2414 (1990).
- ³¹R. P. Sharma, L. E. Rehn, P. M. Baldo, and J. Z. Liu, Phys. Rev. Lett. **62**, 2869 (1989).
- ³²J. Mustre de Leon, S. D. Conradson, I. Batistic, and A. R. Bishop, Phys. Rev. Lett. 65, 1675 (1990).
- ³³A. R. Armstrong, W. I. F. David, I. Gameson, P. P. Edwards, J. J. Capponi, P. Bordet, and M. Marezio, Phys. Rev. B **52**, 15 551 (1995).
- ³⁴R. Åkesson, I. Persson, M. Sandstrom, and U. Wahlgren, Inorg. Chem. **33**, 3715 (1994).
- ³⁵ M. C. Krantz, C. Thomsen, Hj. Mattausch, and M. Cardona, Phys. Rev. B **50**, 1165 (1994).
- ³⁶F. Studer, N. Merrien, C. Martin, C. Michel, B. Raveau, and A. Fontaine, Physica C **178**, 324 (1991); S. Li, M. Greenblatt, Y. Jeon, J. Chen, G. Liang, and M. Croft, *ibid.* **173**, 239 (1991).
- ³⁷The thallium ions in Tl₂O₃ are equally distributed over two types of crystallographic sites; regular octahedra $(6d_{TI-O} \approx 2.26 \text{ Å})$ and rhombohedrally distorted octahedra $(2d_{TI-O} \approx 2.13 \text{ Å}, 2d_{TI-O} \approx 2.18 \text{ Å}, \text{ and } 2d_{TI-O} \approx 2.47 \text{ Å})$. And, in the case of Hg, TI-1223, the TI ions are stabilized in the highly distorted octahedra with significant oxygen vacancy.