



## Charge transfer process in $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $Tl_2Ba_2CaCu_2O_8$ thin films probed by polarized X-ray absorption spectroscopy

J.M. Chen <sup>a,\*</sup>, R.G. Liu <sup>a</sup>, R.S. Liu <sup>b</sup>, H.C. Lin <sup>c</sup>, T.M. Uen <sup>c</sup>,  
J.Y. Juang <sup>c</sup>, Y.S. Gou <sup>c</sup>

<sup>a</sup> Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan, ROC

<sup>b</sup> Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

<sup>c</sup> Department of Electrophysics, National Chiao-Tung University, Hsinchu, Taiwan, ROC

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### Abstract

We report high-resolution polarized O 1s X-ray absorption spectra of highly *c*-axis-oriented  $Tl_2Ba_2Ca_2Cu_3O_{10}$  (Tl-2223) and  $Tl_2Ba_2CaCu_2O_8$  (Tl-2212) superconducting thin films. Near the O 1s edge, the low-energy pre-edge peak at 528.3 eV has mainly O  $2p_{xy}$  symmetry, while the pre-edge peak at 529.4 eV has predominantly O  $2p_z$  character. The spectral weight of the pre-edge peak at 528.3 eV, originating from the  $CuO_2$  planes, increases  $\sim 60\%$  from the Tl-2212 to Tl-2223 thin films. Conversely, the high-energy pre-edge peak at 530.3 eV, originating from the TlO planes, is lower in spectral intensity by  $\sim 30\%$  in Tl-2223 as compared to the Tl-2212 thin film. The experimental results clearly demonstrate the pictures of the self doping due to the charge transfer from the  $CuO_2$  layers to the TlO layers. © 1997 Published by Elsevier Science B.V.

### 1. Introduction

It is well known that holes in p-type cuprate superconductors are responsible for superconductivity. In addition, the cuprate superconductors exhibit strong anisotropic features due to their layered structure. These anisotropies are reflected in their electrical and superconducting properties. Therefore the determination of the position of the hole and its symmetry in the high- $T_c$  superconductors has attracted significant attention in order to understand the origin of superconductivity. For many years, soft

X-ray-absorption spectroscopy has been utilized to obtain valuable information about the local density of unoccupied states at both the O and Cu sites in the high- $T_c$  superconductors [1]. In particular, polarization-dependent X-ray absorption measurements are able to provide detailed information on the orbital character of the holes in the hole-doped cuprates. To date there are a number of studies on the symmetries of unoccupied Cu 3d and O 2p states in the high- $T_c$  superconductors [2–8].

It has been shown experimentally that  $Tl_2Ba_2Ca_2Cu_3O_{10}$  (Tl-2223) superconducting thin films have exhibited not only a high  $T_c$  value but also a high critical current density ( $J_c$ ) of  $\sim 5 \times 10^5$

\* Corresponding author.

A/cm<sup>2</sup> at 100 K [9,10]. The Tl-2223 superconducting thin film is therefore considered to be one of the most viable candidates for device application in the newly discovered high- $T_c$  superconductors [11]. Consequently, a wide variety of deposition methods have been adopted to fabricate Tl-2223 thin films. However, the in-situ growth of Tl-2223 thin films has not yet been successful, due to the high volatility and toxicity of the Tl-oxides, making it difficult to control simultaneously both the Tl and oxygen stoichiometry during deposition. As a result, the thin films obtained by various processes not only are polycrystalline, but also usually contain a noticeable amount of secondary impurity phases. Recently, Lin et al. have developed an efficient method to produce high-quality Tl-2223 superconducting thin films [12]. Such a discovery provides the opportunity to accurately probe the electronic structure near the Fermi level of these materials.

In the present study, we report the electronic structures and symmetries of hole states on the oxygen sites of highly *c*-axis-oriented Tl-2223 superconducting thin films deposited on MgO(100) substrates probed by polarization-dependent O 1s X-ray absorption spectroscopy. In addition, in order to understand the variation of electronic structures due to increase in the CuO<sub>2</sub> planes in the double-thallium-layer compounds, polarized O *K*-edge X-ray absorption spectra of the Tl<sub>2</sub>Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> (Tl-2212) thin films have also been carried out in this study. It is observed that an increase of the hole concentrations in the CuO<sub>2</sub> planes is accompanied by a decrease of the 2p hole states in the TlO planes in Tl-2223 as compared to the Tl-2212 thin film. The experimental results clearly demonstrate the pictures of the internal redox process arising from the charge transfer from the CuO<sub>2</sub> layers to the TlO layers.

## 2. Experimental

Detailed procedures for producing Tl-2223 superconducting thin films have been reported in detail elsewhere [12], so only pertinent details will be given here. Precursor films with thickness of  $\sim 1 \mu\text{m}$  were deposited on MgO(100) single-crystalline substrates by dc sputtering from a pre-sintered target of Tl:Ba:Ca:Cu with 2:2:2:3 stoichiometry. The as-de-

posited precursor films were then wrapped with a bulk Tl-2223 pellet using gold foil and sealed with  $\sim 1$  atm of pure oxygen in a quartz tube. Subsequently, the whole assembly was put into a tube furnace at room temperature. As the severe temperature fluctuations may significantly affect the quality of the superconducting thin films, the furnace temperature was programmed and computer controlled. The sample was heated up to 910°C at a heating rate of 10°C/min and immediately cooled with a rate of 0.3°C/min to 900°C, and then to 600°C within a period of 30 min. The sample was then cooled to room temperature in the furnace. The Tl-2223 thin films prepared by this procedure are single phase and highly preferentially oriented with the *c*-axis perpendicular to the surface of the thin films as checked by X-ray diffraction (XRD). The highly *c*-axis-oriented Tl-2212 thin films were prepared by similar procedures but with a low postannealing temperature at  $\sim 900^\circ\text{C}$ .

The polarization-dependent X-ray absorption experiments were carried out at the Synchrotron Radiation Research Center (SRRC) with an electron beam energy of 1.5 GeV and a maximum stored current of 240 mA. The radiation was monochromatized by the 6-m high-energy spherical grating monochromator (HSGM) which covered the photon energy range of 150–1200 eV. The polarized X-ray absorption spectra with several incidence angles ( $\phi$ ) with respect to the normal the sample surface were recorded by rotating the sample around a vertical axis. As we used narrow slits centered around the orbit plane, the linear polarization of the monochromatic beam was estimated to be around 97%. The X-ray-fluorescence yield spectra were obtained using a microchannel plate (MCP) detector [13]. In contrast to the electron-yield measurements, the X-ray-fluorescence yield measurement is strictly bulk sensitive with a probing depth of thousands of ångström. The MCP detector consists of a dual set of MCP's with an electrically isolated grid mounted in front of them. For X-ray fluorescence yield detection, the grid was set to a voltage of 100 V, while the front of the MCPs was set to  $-2000$  V, and the rear to  $-200$  V. The grid bias insured that positive ions would not be detected while the MCP bias insured that no electrons were detected. The incident photon intensity ( $I_0$ ) was measured simultaneously by a Ni mesh

located after the exit slit of the monochromator. All the measurements were normalized to  $I_0$ . The photon energies were calibrated using the O  $K$ -edge absorption peak at 530.1 eV of the CuO compound. The energy resolution of the monochromator was set to  $\sim 0.22$  eV at the O 1s absorption edge.

### 3. Results and discussion

In Fig. 1 the O  $K$ -edge X-ray absorption spectra of the Tl-2223 superconducting thin film as a function of different incidence angles ( $\phi$ ) are shown, obtained using a bulk-sensitive total-X-ray-fluorescence yield method. The absorption spectrum for  $\phi = 0^\circ$  corresponds to the normal incidence geometry where the electric field vector  $E$  of the linear-polarized synchrotron light is parallel to the  $ab$  plane of the thin film, while the spectrum for  $\phi = 75^\circ$

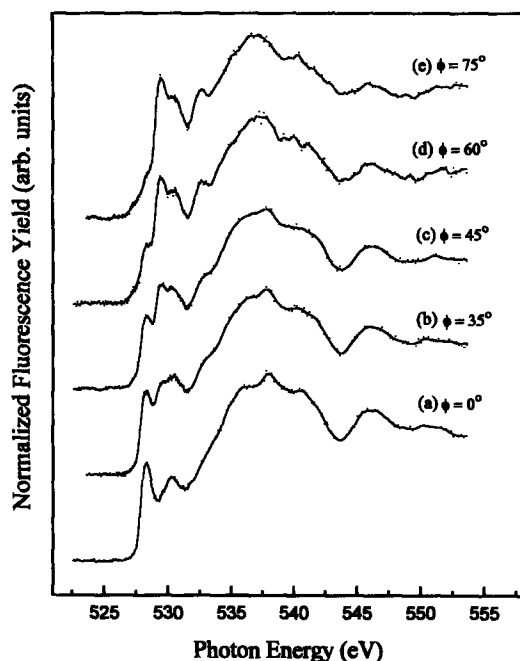


Fig. 1. Polarization-dependent O  $K$ -edge X-ray absorption spectra of the Tl-2223 superconducting thin film as a function of the incidence angle  $\phi$  with respect to the normal of the sample surface. The absorption spectrum for  $\phi = 0^\circ$  corresponds to the electric field vector  $E$  of the synchrotron light parallel to the  $ab$  plane of the thin film, while spectrum for  $\phi = 75^\circ$  represents the  $E$  vector nearly parallel to the  $c$ -axis of the thin film.

represents the grazing incidence geometry where the  $E$  vector is nearly parallel to the  $c$ -axis of the thin film. 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 [1]. The O 1s X-ray absorption spectra for the Tl-2223 superconducting thin film, as shown in Fig. 1, can be divided into two regions: below and above the photon energy  $\sim 532$  eV. The low-energy pre-edge peaks with energy below 532 eV are ascribed to transitions from the O 1s core electrons to holes with 2p symmetry on the oxygen sites, while the strong rise in spectral weight of the absorption spectra above 532 eV is attributed to continuum absorption to Tl 6p, Ba 5d, Ca 3d, and Ba 4f empty states hybridized with O 2p states [14]. The prominent features in the O 1s X-ray absorption edge for  $E\|ab$ , as shown in Fig. 1a, are two strong pre-edge peaks at 528.3 and 530.3 eV, respectively. For  $\phi = 35^\circ$ , as shown in Fig. 1b, another pre-edge peak near 529.4 eV is observed. The intensity of low-energy pre-edge peak at 528.3 eV decreases when the incidence angle of the light increases and almost diminishes at  $\phi = 75^\circ$ , as shown in Fig. 1e. This indicates that this pre-edge peak has predominantly O  $2p_{xy}$  symmetry. Conversely, the intensity of the pre-edge peak at 529.4 eV increases on going from  $E\|ab$  to  $E\|c$  polarization, showing that this pre-edge peak has mainly O  $2p_z$  symmetry. In addition, it is noted from Fig. 1a–d that the intensity of the pre-edge peak at 530.3 eV slowly increases with increasing incidence angle of light.

Fig. 2 presents the schematic crystal structure of the Tl-2223 compound. It consists of three  $\text{CuO}_2$  layers (separated by Ca layers) and of rock-salt type  $\text{Tl}_2\text{O}_2$  layers, where the  $\text{CuO}_2$ –Ca– $[\text{CuO}_2]$ –Ca– $\text{CuO}_2$  layers are separated by single BaO layers from the  $\text{Tl}_2\text{O}_2$  layers. As shown, there exist four nonequivalent oxygen sites in Tl-2223, O(1) and O(1') within the  $\text{CuO}_2$  layers of the square planar and pyramidal arrangements, respectively, O(2) in the BaO planes, and O(3) in the TlO planes. Based on the local-density approximation band-structure calculations of  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-\delta}$  by Marksteiner et al., these different O sites are predicted to have three different binding energies for the O 1s level [15]. The O(3) atoms in the TlO planes are predicted

to have the largest binding energy of the O 1s level. The O 1s binding energy of the O(2) atoms is 1.2 eV smaller than that of the O(3) atoms. Finally, the O 1s energy levels of the O(1) and O(1') atoms are predicted to be  $\sim 1.2$  eV smaller than that of the O(2) atoms. Utilizing this result, one can ascribe the first absorption peak at 528.3 eV with mainly O  $2p_{xy}$  symmetry, as shown in Fig. 1, to the excitations of O 1s electrons to O 2p holes located in the O(1) and O(1') atoms within the  $\text{CuO}_2$  planes, the second peak at 529.4 eV with predominantly O  $2p_z$  symmetry to O 2p holes in the O(2) atoms within the BaO planes and the third peak at 530.3 eV to O 2p holes in the O(3) atoms within the TlO planes. The same assignment has been proposed on the basis of the O 1s X-ray absorption spectra of the polycrystalline Tl-2223 superconductor [16]. The present experiments clearly reveal a Fermi edge due to mainly O  $2p_{xy}$  states from the  $\text{CuO}_2$  planes and due to predominantly O  $2p_z$  states from the BaO planes. The results are similar to those obtained from the Tl-2223

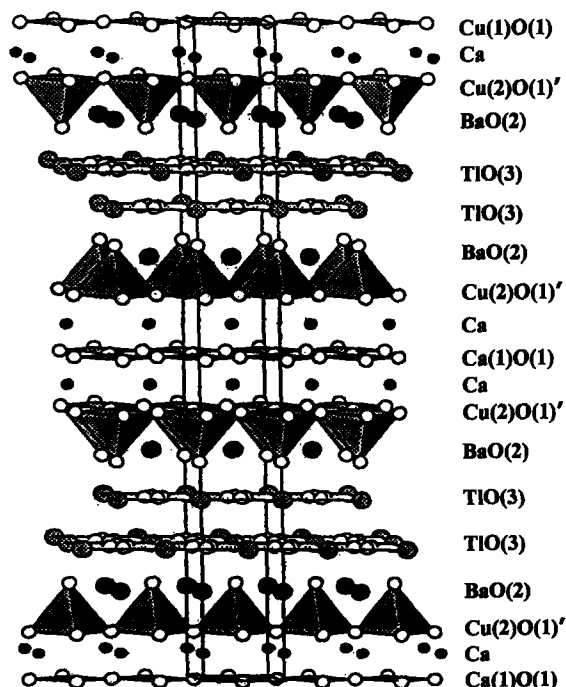


Fig. 2. A schematic representation of the crystal structure of the  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (Tl-2223) compound. Oxygen in the  $\text{CuO}(1)$  planes,  $\text{CuO}(1')$  planes, apical sites, and TlO planes are denoted by O(1), O(1'), O(2), and O(3), respectively.

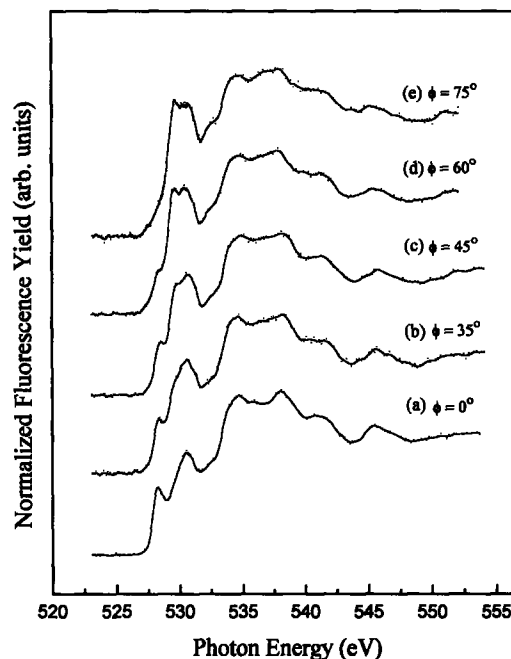


Fig. 3. Polarization-dependent O  $K$ -edge X-ray absorption spectra of the Tl-2212 superconducting thin film recorded at different incidence angles  $\phi$  with respect to the  $c$ -axis of the thin film.

single crystal [17]. In addition, the observation of the O(3) hole states supports the metallic character of the TlO layers.

In Fig. 3, polarized O  $K$ -edge X-ray absorption spectra of the Tl-2212 superconducting thin film recorded at different incidence angles ( $\phi$ ) with respect to the  $c$ -axis of this film were shown. The principal structures of the O 1s absorption spectrum in the Tl-2212 thin film for the incidence angle  $\phi = 45^\circ$ , as shown in Fig. 3c, are three distinct pre-edge peaks centered at 528.3, 529.5 and 530.6 eV, respectively. The intensity of the pre-edge peak at 528.3 eV increases on going from  $E||ab$  to  $E||c$  polarization, while the intensity of the pre-edge peak at 529.5 eV displays an opposite polarization dependence. This implies that the low-energy pre-edge peak at 528.3 eV has mainly O  $2p_{xy}$  symmetry and the pre-edge peak at 529.5 eV has predominantly O  $2p_z$  symmetry. In analogy to the Tl-2223 system, we ascribed these pre-edge peaks to the transitions into O 2p holes located in the  $\text{CuO}_2$  planes, BaO planes, and TlO planes, respectively. This assignment is in agreement with recent O  $K_\alpha$  X-ray emission mea-

measurements on the polycrystalline Tl-2212 superconductor [18]. This assignment is also supported by the local-density approximation band-structure calculations [15].

For comparison, the O 1s X-ray absorption spectra of the Tl-2212 and Tl-2223 thin films for the incidence angle  $\phi = 0^\circ$  are displayed in Fig. 4. The O *K*-edge absorption spectra in Fig. 4 have been normalized between 544 and 555 eV with respect to the number of O atoms per unit cell, providing the absolute intensities of the pre-edge peaks for the Tl-2212 and Tl-2223 compounds. This is due to the fact that the spectra above 544 eV for the Tl-2212 and Tl-2223 thin films are quite similar and independent of the different oxygen environments.

As seen from Fig. 4, the spectral weight of the low-energy pre-edge peak at 528.3 eV increases by  $\sim 60\%$  from the Tl-2212 to the Tl-2223 thin films. This indicates that the average number of holes on O(1) or O(1') sites per CuO<sub>2</sub> plane is about the same for both Tl systems. Conversely, the high-energy pre-edge peak originating from the TlO planes is lower in spectral intensity by  $\sim 30\%$  in the Tl-2223

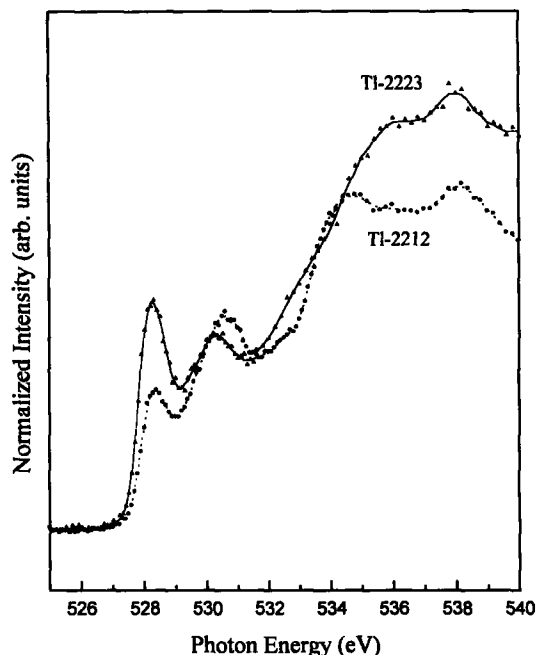


Fig. 4. O 1s X-ray absorption spectra of Tl-2212 (solid circles) and Tl-2223 (solid triangles) thin films for the electric field vector *E* parallel to the *ab* plane of the thin film.

as compared to the Tl-2212 thin film. In the single-thallium-layer compounds of TlBa<sub>2</sub>Ca<sub>*n*-1</sub>Cu<sub>*n*</sub>O<sub>2*n*+3</sub> (*n* = 1–5), each Tl has four near neighbor Tl atoms as compared to eight in the double-thallium-layer-compounds in Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>*n*-1</sub>Cu<sub>*n*</sub>O<sub>2*n*+4</sub> (*n* = 1–4). Enhanced Tl–Tl interactions in the double-thallium-layer materials are expected to increase the Tl 6s band width as compared to that in the single-thallium-layer compounds. According to a tight-binding calculation, the Tl 6s band of the double-thallium-layer compounds of Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>*n*-1</sub>Cu<sub>*n*</sub>O<sub>2*n*+4</sub> is sufficiently broad and lies significantly below the Fermi level [19,20]. Consequently, the Tl 6s band overlaps extensively with the CuO<sub>2</sub> band. It is therefore expected that there exists the charge transfer from the CuO<sub>2</sub> layers to the TlO layers in the double-thallium-layer materials. This internal redox mechanism gives rise to both holes (in the CuO<sub>2</sub> layers) and electrons (in the TlO layers) via Tl<sup>3+</sup> + [Cu–O]<sup>0</sup> → Tl<sup>[3- $\delta$ ]<sup>+</sup> + [Cu–O] <sup>$\delta$ +</sup>. This is in agreement with the band-structure calculations on the double-thallium-layer compounds [21]. Electron pockets at the *T* and *Z* point of the Brillouin zone are formed from an antibonding bond composed of O(2) 2p (in the BaO planes) and O(3) 2p orbitals (in the TlO planes) hybridized with Tl 6s and Tl 5d<sub>3z<sup>2</sup>-r<sup>2</sup></sub> orbitals. This result is also consistent with the observation of charge transfer Tl<sup>[3- $\delta$ ]<sup>+</sup> – [Cu–O] <sup>$\delta$ +</sup> in Tl<sub>2</sub>Ba<sub>2</sub>CuO<sub>6</sub> and Tl-2223 by X-ray photoemission spectroscopy of the Tl 4f core levels [22,23].</sup></sup>

Therefore, it is expected that an increase of O 2p hole states in the CuO<sub>2</sub> planes on the Tl-2223 compound due to the insertion third CuO<sub>2</sub> layers have to be counterbalanced by additional charge transfer from the TlO planes to the CuO<sub>2</sub> planes and consequently a decrease of O 2p hole states in the TlO planes. As shown in Fig. 4, the present O *K*-edge X-ray absorption spectra provide evidence for such a decrease of the O 2p hole states in the TlO planes when going from the Tl-2212 to Tl-2223 thin films. In addition, as seen from Fig. 4, the peak originating from the TlO plane is shifted to lower energy by  $\sim 0.3$  eV from the Tl-2212 to Tl-2223 thin films. This implies that the effective ionic valence of the TlO layers in Tl-2212 is higher than that in Tl-2223. Our experimental results, therefore, clearly support the pictures of the self doping due to charge transfer from the CuO<sub>2</sub> layers to the TlO layers.

#### 4. Conclusions

Using polarization-dependent O 1s X-ray absorption measurements, symmetries of the hole states near the Fermi level of highly *c*-axis-oriented TI-2223 and TI-2212 superconducting thin films have been determined. Near the O 1s absorption edge, three distinct pre-edge peaks for both systems were clearly revealed. The low-energy pre-edge peak centered at 528.3 eV has mainly O 2p<sub>xy</sub> symmetry, while the pre-edge peak at ~529.4 eV has predominantly O 2p<sub>z</sub> symmetry. These three pre-edge peaks were attributed to the O 1s excitations to O 2p holes located in the CuO<sub>2</sub> planes, BaO planes, and TlO planes, respectively. An increase of the O 2p<sub>xy</sub> hole states in the CuO<sub>2</sub> planes is accompanied by a decrease of the 2p hole states in the TlO planes in TI-2223 as compared to the TI-2212 thin film. The experimental results clearly demonstrate the pictures of the internal redox process due to charge transfer from the CuO<sub>2</sub> layers to the TlO layers.

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