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A polarized x-ray absorption spectroscopy study of O K and Cu L₃ edges in a Tl(2212) thin film

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Abstract. A reliable estimate of the density of states having in-plane and out-of-plane symmetry in the O K-edge and the Cu L₃-edge polarized spectra is important for checking the validity of several theoretical models which predict an active role for these states in the mechanism of superconductivity. In the present contribution, we report on our fluorescence-yield O K-edge and Cu L₃-edge polarized spectra obtained for a well characterized and oriented overdoped Tl(2212) thin film as well as our simultaneous fluorescence- and total-yield Cu L₃ measurements on an optimally doped Tl(2212) thin film. Our results show that a significant number of out-of-plane O 2p_z and Cu 3d_{z²-r²} holes also exist in thallium cuprates, more so in the overdoped case, and that use of the bulk-sensitive fluorescence technique is better for obtaining a reliable estimate of the density and symmetry of these holes. The spectra are compared with those reported earlier for other cuprate systems and are interpreted in terms of the available band-structure calculations. No direct correlation between superconductivity and the presence or absence of out-of-plane covalent and doping hole densities appears plausible, so theories based on the existence of a large density of such holes appear to be inconsistent with the experiment.

1. Introduction

X-ray absorption spectroscopy and allied high-energy spectroscopy techniques have proved to be of great use in the study of the important question of the symmetry of the itinerant doping holes in various cuprate systems responsible for superconductivity; see, e.g., [1–14]. Most reports seem to agree that the O 2p and the Cu 3d holes have a predominantly in-plane symmetry, but with a significant population of out-of-plane O 2p holes. However, there is no such consensus on the existence of out-of-plane Cu 3d_{z²-r²} holes, and the estimates of their weight vary from 0% to 20% for different high-*T_c* compounds. For example, a number of studies [4, 8] carried out on the Bi(2212) system using the total-yield (TY) detection mode have reported a substantial weight for these, along with a shift of the main peak by about 400 meV to higher energy. Nucker *et al* [5] reported a similar result for the YBCO(123) system from their EELS study. Chen *et al* [7] have, however, convincingly shown from their fluorescence-yield (FY) study of the La_{2-x}Sr_xCuO₄ system that while both the covalent and the doping holes possess a significant O 2p_z character, likely to be associated with the apical O, the Cu 3d_{z²-r²} states are virtually absent. Later on, studies carried out using bulk-sensitive fluorescence detection [11, 12, 14] also indicated the virtual

absence of these states from Bi(2212). Just when a consensus seemed to be emerging on the absence of Cu $3d_{z^2-r^2}$ holes when the measurements are done using the FY mode, Pellegrin *et al* [9] demonstrated the presence of a significant population of these states in the Tl(2223) system with the FY mode. The question of the presence or absence of the Cu $3d_{z^2-r^2}$ holes and their relevance, if any, to superconductivity thus continues to hold interest for both theoretical study and experiments in this field.

Several multi-band models that advocate an active role for the Cu $3d_{z^2-r^2}$ and O $2p_z$ orbitals, and the three-band model which uses only in-plane Cu $3d_{z^2-r^2}$ and O $2p_{x,y}$ orbitals, have been proposed for describing the transport properties both for normal and for superconducting states of high- T_c cuprate superconductors. Muller [15] has proposed an enhancement of T_c by the anharmonicity of the vibrations of apical oxygens. The importance of Cu $3d_{z^2-r^2}$ -O $2p_z$ hybrids has been stressed by Anisimov *et al* [16]. On the other hand, there are models which predict the presence of out-of-plane orbitals to be detrimental to superconductivity. Ohta *et al* [17] found a correlation between T_c and the energy difference between apical O $2p_z$ states and planar O $2p_{x,y}$ states. Similarly, Di Castro *et al* [18] point out that the highest critical temperature can be achieved in the compounds for which the interaction between apical oxygen(s) and the CuO₂ plane is the weakest. Grant and McMahan [19] have stressed the importance of apical O $2p_z$ in determining the nature and the dispersion of quasiparticle states of p-type-doped cuprates. The question of whether a multi-band approach is required has also been discussed by Eskes and Sawatzky [20].

In the present contribution, we report the results of our $E\parallel(a, b)$ and $E\parallel c$ measurements carried out at the O K and the Cu L₃ edges for an overdoped Tl(2212) thin film using the fluorescence-yield detection mode and those carried out at the Cu L₃ edge for an optimally doped Tl(2212) thin film simultaneously using both the FY and the TY modes. These measurements have been done: (i) to provide reliable XAS data in respect of the Tl(2212) system, (ii) to allow us to comment on the adequacy of the various existing theoretical models in the light of our results and (iii) to throw some light on the discrepancies and disagreements in the data obtained using the FY and the TY detection modes for the various systems.

2. Experimental procedure

The thin films were deposited on oriented LaAlO₃(100) substrates by multi-target sputtering. The gas pressure was maintained at 10^{-2} mbar for Ar and 10^{-3} mbar for oxygen. The substrate was not heated due to the high volatility of Tl₂O. After the deposition, the films were annealed in order to crystallize the 2212 phase. Both of the films were annealed under high oxygen pressure (70 bar). Thereafter, to optimize the doping hole density as well as T_c , one of the films was post-annealed under an Ar flow at 180 °C for ten minutes. As it turns out, the post-annealed film was optimally doped and the as-prepared film was found to be overdoped. The details of the deposition process are described elsewhere [21]. The films were found to be monophasic by x-ray diffraction and exhibit homogeneous platelets with the c -axis perpendicular to the substrate plane. The magnetic susceptibility data indicated a T_c of 105 K for the optimally doped film and 100 K for the other.

The Cu L₃ and O K XAS measurements were performed on the overdoped film at the Dragon beamline of AT&T at NSLS, Brookhaven. A high-sensitivity seven-element Ge detector was used to record the spectra in the FY mode and an azimuthal rotation was used to achieve a complete polarization geometry and to eliminate the optical path variation [7]. The Cu L₃-edge spectra for the other film (optimally doped) were recorded simultaneously in both the TY and the FY modes on the SA32 beamline of the SUPER ACO facility at

LURE, Orsay.

A standard procedure was adopted to remove the background contribution from the spectra and then the spectra recorded in the fluorescence detection mode were corrected for self-absorption effects employing the method of Troger *et al* [22]. The spectra were then normalized at points sufficiently far away from the regions in which changes in intensity are expected. The relative intensities of the various peaks in the O K and the Cu L₃ spectra were determined by simulating the spectra with a combination of Gaussian and Lorentzian functions in a program used to fit neutron diffraction line profiles. The program was modified to take into account the specificities of the x-ray absorption data and to introduce linewidth per peak as a fitted parameter.

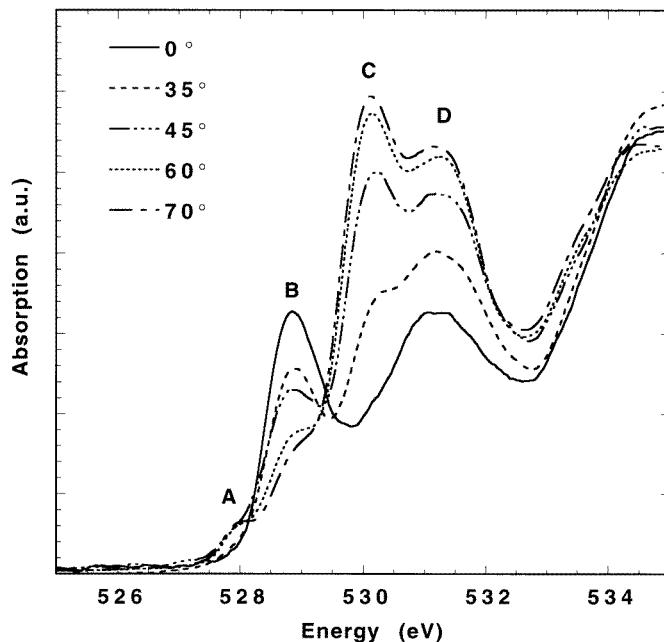


Figure 1. The O K-edge spectra taken for the as-prepared Tl(2212) thin film using the fluorescence detection mode for different orientations of the sample surface with respect to the incident electric field vector E .

3. Results and discussion

3.1. The O K edge of the as-prepared film (FY-mode detection)

Polarized x-ray absorption spectroscopy at the O K edge has proved to be a powerful tool for probing the nature and symmetry of the hole states in the superconducting cuprate perovskites. Figure 1 shows our polarized O K-edge spectra recorded in the FY mode for the as-prepared Tl(2212) thin film at different orientations of the film surface (i.e. the (a, b) plane) with respect to the incident electric field vector E . While the 0° spectrum indicates the $E \parallel (a, b)$ case and probes the O $2p_{x,y}$ symmetric hole states, the 90° spectrum indicates the $E \parallel c$ case and probes the states with O $2p_z$ character.

The $E \parallel (a, b)$ spectrum, in general, consists of, amongst others, two main features—a peak (called a pre-peak) at 528.8 eV and a broad structure at around 531.2 eV. As can be

Table 1. The intensities of the peaks A, B and C observed at the O K edge of the as-prepared Tl(2212) thin film in the FY mode. The intensities are normalized with respect to the total area under the features A, B, C and D of the edge shown in figure 1. θ is the angle between the electric field vector \mathbf{E} and the (a, b) plane of the film. Asterisks mark the values obtained from extrapolation.

θ (deg)	Peak A	Peak B	Peak C
0	0	0.34	0.09
35	0	0.24	0.20
45	0.01	0.15	0.38
60	0.015	0.10	0.42
70	0.018	0.07	0.44
90*	0.02*	0.015*	0.52*

seen from figure 1, changing the polarization from $\mathbf{E} \parallel (a, b)$ to $\mathbf{E} \parallel c$ drastically decreases the intensity of the 528.8 pre-peak but greatly enhances the intensity of the broad structure which, in fact, now splits up into two peaks (C and D) located at 530.1 and 531.2 eV respectively. Also, a new small feature emerges at 527.8 eV which can be clearly seen in the $\mathbf{E} \parallel c$ polarization only. To estimate the intensities of the peaks at 527.8 eV (A), 528.8 eV (B), 530.1 eV (C) and 531.2 eV (D), a common arctangent-like background has been subtracted from the experimental spectra in the energy range 525–534 eV, following a procedure adopted by Chen *et al* [23]. The resulting data have been fitted by a mixture of Gaussian and Lorentzian line-shapes to allow us to estimate the intensities of the four peaks as a function of the orientation. The orientation dependence of the most significant three of these (A, B and C) can be seen from the corresponding intensity values which are given in table 1.

Local density approximation (LDA) band-structure calculations [24] have shown that relative to the Fermi edge the binding energy of the O(1) 1s level turns out to be the lowest while those for the O(2) and O(3) 1s levels are respectively 1.2 and 2.2 eV higher. These calculated chemical shifts are found to be in good agreement with the photoemission and x-ray absorption measurements reported on Tl cuprates [25–27] and can be used to explain the various features observed in the polarized spectra. The pre-peak (B) in the $\mathbf{E} \parallel (a, b)$ spectrum is attributed to transitions into the unoccupied in-plane O(1) $2p_{x,y}$ states. These empty states represent the oxygen contribution to the doping hole densities, as described through the $|3d^9\bar{L}\rangle$ representation, and refer to the ligand band in the effective one-band Hubbard model extended to the O K edge [23]. Its relative intensity compared to that of the broad structure at 531.2 eV (peak D) is higher than that observed for underdoped and optimally doped Tl(2212) by Pellegrin *et al* [25], and thus confirms the overdoped nature of the thin film used in this experiment. As shown in figure 1, the intensity of the pre-peak (B) decreases sharply with increasing angle between the incident electrical field and the (a, b) plane of the Tl(2212) film. Using a dipolar angular variation of the form

$$I_{|2p^6\rangle}(0^\circ) \cos^2 \theta + I_{|2p^6\rangle}(90^\circ) \sin^2 \theta$$

the intensities of the various peaks have been extrapolated for the $\theta = 90^\circ$ case, i.e. the $\mathbf{E} \parallel c$ incidence case. As can be seen from table 1, the intensity of peak B is quite small, showing that only a very small number of hole states have O $2p_z$ symmetry. On the other hand, the large intensity of the pre-peak (B) in the $\mathbf{E} \parallel (a, b)$ spectrum clearly indicates that a large majority of these hole states have O $2p_{x,y}$ character. The features observed at 530.1 eV (peak C) and 531.2 eV (peak D) in the spectrum recorded at 70° incidence

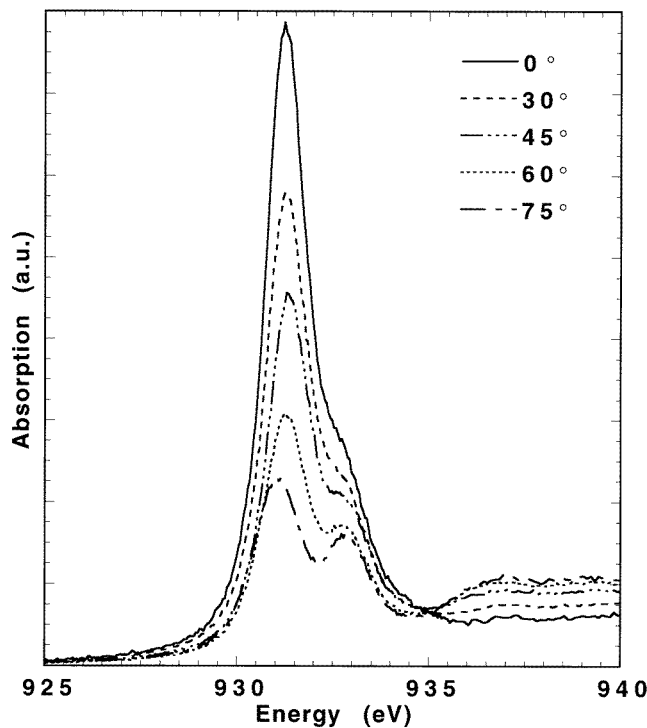


Figure 2. The Cu L₃-edge spectra of the as-prepared film taken using the fluorescence-yield detection mode for different orientations of the sample surface and the incident electric field vector E .

could be ascribed to O(2) and O(3) 2p states respectively [28, 24]. Also, according to these LDA calculations, the essential contribution to the spectral weight for O(2) and O(3) atoms comes from the states forming narrow peaks in the 2p density of states (DOS). These DOS near the Fermi level consist of O(2)–Tl–O(3) bands formed by the hybridization of Tl 6s and Tl 5d_{3z²-r²} orbitals and O(2) and O(3) 2p_z orbitals, and therefore have a predominantly O 2p_z character. The hybridization is quite strong due to relatively short distances between the Tl and apical O atoms (Tl–O(2) = 2.05 Å and Tl–O(3) = 2.42 Å).

The high intensity of the pre-peak (C) for the 70° orientation in figure 1 shows the predominantly O(2) 2p_z symmetry of these states. This could be explained by considering the short Tl–O(2) distances and the resulting strong charge transfer from the apical oxygen O(2) and, to a smaller extent, from the oxygen O(3) to the Tl along the c -axis. Earlier polarized XAS at the Tl L₃ edge on the same film also indicated this [29, 30]. The band-structure calculations for this system [24] also predict that the electron pockets at E_F are formed from an antibonding band composed of the O(2) 2p_z and O(3) 2p_z orbitals hybridized with the Tl 6s and the Tl 5d_{3z²-r²} orbitals.

The intensity of the D peak at 531.2 eV corresponding to the Tl–O(3) bond is also found to increase with the angle of incidence (figure 1) and is also large as compared to the ones reported for underdoped and optimally doped Tl(2212) thin films and single crystals [25]. This suggests that extra oxygens could be stabilized in the Tl–O layers in synthesis under high oxygen pressure. The origin of the large D peak in the $E \parallel (a, b)$ spectrum is not so clear. As suggested by Pellegrin *et al* [25], it may be composed of states with O 2p_{x,y}

character originating from the upper Hubbard band (UHB) related to CuO_2 planes and the oxygens O(2) and/or O(3). In our spectrum, the contribution from O(3) states appears to be larger than that from the O(2) states.

The peak A appearing at about 527.8 eV (see figure 1) for incident angles larger than 45° has not been reported earlier for Tl cuprates, but a similar feature at 527.2 eV is observed in the out-of-plane EELS spectra of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [31] and has been ascribed to O(4) $2p_z$ in the 1–2–3 unit cell which is predicted to have the lowest binding energy from band-structure calculations [32–34]. In the Tl(2212) case this feature may be attributed to the O $2p_z$ states hybridized with the Cu $3d_{z^2-r^2}$ orbitals, which may be pushed closer to the Fermi level for the $|3d_{z^2-r^2}^9\rangle$ configuration. However, this needs to be further examined experimentally.

Table 2. The densities of the covalent and the doping holes in the as-prepared Tl(2212) thin film. The $3d^9$ and $3d^9\bar{\underline{L}}$ contributions are calculated taking the intensity of the line $|3d^9\rangle$ in the 0° spectra as 100. θ is the angle between the electric field vector \mathbf{E} and the (a, b) plane of the film and n_h represents the density of holes per copper site. Asterisks mark the values obtained from extrapolation.

Sample	T_c (K)	θ (deg)	$3d^9$	$3d^9\bar{\underline{L}}$	n_h
Tl(2212)	100	0	100	37.5	0.27
		30	70	28	0.28
		45	48.5	20.5	0.30
		60	34	16	0.32
		75	22.5	13	0.37
		90*	13*	10*	0.44*

Table 3. Comparison between the density of the covalent ($|3d^9\rangle$) and the doping ($|3d^9\bar{\underline{L}}\rangle$) holes in the post-annealed Tl(2212) thin film obtained using TY and FY detection modes (figure 3). The $3d^9$ and $3d^9\bar{\underline{L}}$ contributions are calculated taking the intensity of the line $|3d^9\rangle$ in the 0° spectra as 100. θ is the angle between the electric field vector \mathbf{E} and the (a, b) plane of the film and n_h represents the density of holes per copper site. Asterisks mark the values obtained from extrapolation.

Sample	T_c (K)	θ (deg)	Total yield			Fluorescence yield		
			$3d^9$	$3d^9\bar{\underline{L}}$	n_h	$3d^9$	$3d^9\bar{\underline{L}}$	n_h
Tl(2212)	105	0	100	20.5	0.17	100	23.5	0.19
		35	70.7	13.0	0.16	67.5	15.2	0.18
		70	29.7	3.7	0.11	23.7	4.3	0.15
		90*	19.0*	1.0*	0.05*	12.0*	1.0*	0.07*

3.2. The Cu L_3 edge of the as-prepared film (FY-mode detection)

The Cu L_3 spectra recorded by us at NSLS, Brookhaven, for the as-prepared film, are shown in figure 2. The intensities of the Cu $|3d^9\rangle$ and Cu $|3d^9\bar{\underline{L}}\rangle$ peaks determined by the method of curve fitting described above are given in table 2. The densities of doping holes for various orientations were then calculated with the help of the relation

$$n_h = I_{|3d^9\bar{\underline{L}}\rangle} / (I_{|3d^9\bar{\underline{L}}\rangle} + I_{|3d^9\rangle})$$

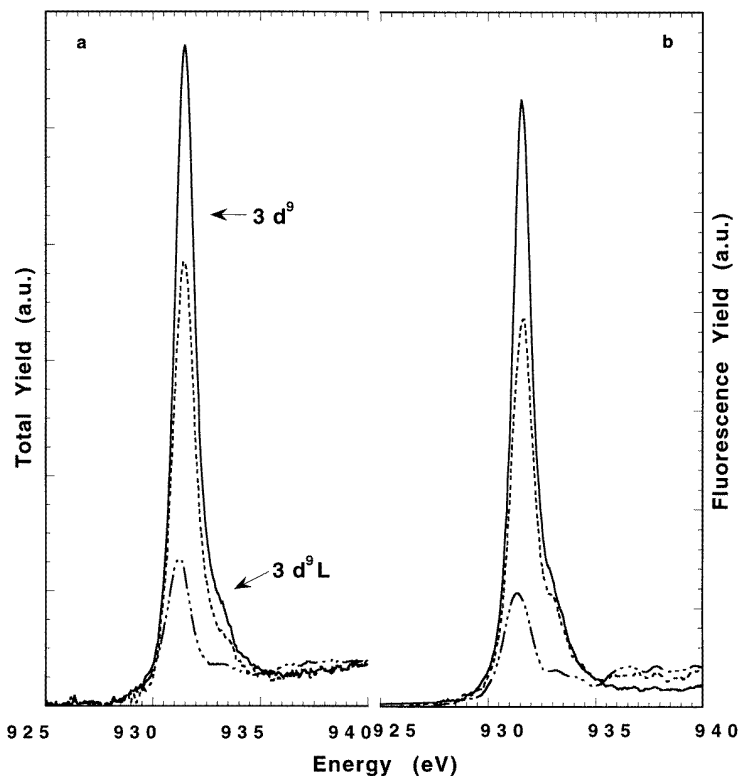


Figure 3. The Cu L₃-edge spectra of the post-annealed Tl(2212) thin film simultaneously recorded using the TY and FY modes of detection are shown in panels (a) and (b) respectively. The solid line represents the spectrum taken at 0°, the dotted line that taken at 35° and the chain line that for the 70° orientation.

wherein n_h , it must be pointed out, gives the number of doping holes as a fraction of the total number of holes (doping and covalent) present in that particular orientation and \underline{L} stands for a hole in the oxygen ligand orbital induced by doping; these are shown in table 2.

First of all, it can be easily seen from the table 2 that the intensity of the $|3d^9\underline{L}\rangle$ peak and the doping hole density are not only not zero but are significant even in the $\mathbf{E}\parallel c$ case, which establishes beyond any reasonable doubt that some Cu $3d_{z^2-r^2}$ doping holes are definitely present. We have already seen the same in the case of the O $2p_z$ holes. This means that the theoretical models that depend on the absence of holes with out-of-plane symmetry [17, 18] receive no support from the experiment. As for the other models that advocate a positive role for them, it is difficult to make a conclusive statement in view of the fact that there are some systems like LSCO and Bi(2212) in which their weight is insignificant but the systems are still superconductors.

Another important finding from our experiments is that no energy shift is observed for either of the peaks Cu $|3d^9\rangle$ or Cu $|3d^9\underline{L}\rangle$ in the spectra recorded in the FY mode, which is in disagreement with most of the reported spectra recorded using the TY detection mode. We return to this point later. From table 2, it can also be seen how the density of doping holes fraction n_h increases as we go from the $\mathbf{E}\parallel(a, b)$ to the $\mathbf{E}\parallel c$ polarization even as the total number of holes tends to sharply decrease. This is also clearly borne out by the spectra in figure 2.

3.3. FY and TY spectra of the Cu L₃ edge from the post-annealed film

The Cu L₃-edge spectra of the optimally doped Tl(2212) thin film, recorded at room temperature simultaneously in the TY and FY modes for three different orientations are respectively shown in figures 3(a) and 3(b). The relative intensities of the |3d⁹_↑) and the |3d⁹_↓) peaks for the TY and the FY spectra (obtained from the fitting procedure and the dipolar extrapolation method described above), and also the doping hole densities (n_h) for the TY and FY cases, are given in table 3.

As can be seen from the above, there is very little agreement between the data from the TY and the FY detection modes—the relative intensity of |3d⁹_↑) is higher for each orientation in the TY mode but for |3d⁹_↓) exactly the reverse is the case. The doping hole density (n_h) is always higher in the FY mode. It is, therefore, apparent that the two techniques do not give identical results. While the TY mode may be regarded as at least partially surface sensitive (more so in the case of the grazing incidence, i.e. the $\theta = 0^\circ$ case), the FY spectra also need to be precisely corrected for the self-absorption effects. A further complication may arise in the TY spectra recorded in the present case because of the fact that the surface of the film has not been cleaned in the experiment to avoid possible damage to it from sputtering. Under these circumstances, when the surface of a thin/thick film or a crystal cannot be cleaned/cleaved, the FY mode may be a safer option.

Acknowledgments

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