Role of out-of-plane copper orbitals in thallium cuprate

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To understand the role of out-of-plane copper orbitals, polarization dependent measurements of Cu L_3-absorption edge on well characterized Tl(2212) thin films have been performed. The density of unoccupied states having $3d_{z^2-r^2}$ character is found to depend on the amount of doping suggesting that out-of-plane copper orbitals essentially play a role of hole reservoir. The energy shift in the positions of white lines of $E\|(a,b)$ and $E\|c$ spectra is also found to be doping dependent. The probable reason for the observed shift is discussed. [S0163-1829(96)10226-5]

I. INTRODUCTION

High energy spectroscopic techniques have played a vital role in understanding the electronic structure of high-T_c superconductors.[1] There seems to be an agreement that both Cu $3d$ and O $2p$ holes have predominantly in-plane symmetry. However, there is no consensus on the existence and role of density of holes having out-of-plane character. It is important to study the role of these out-of-plane orbitals as several multiband models which assume an active role of holes having Cu $3d_{z^2-r^2}$ and O $2p_z$ symmetries have been proposed.[2–10] While some of them depend on the presence of Cu $3d_{z^2-r^2}$ and O $2p_z$ states for superconductivity,[2–6] there are others which predict that, if present, these states would be detrimental to the cause of superconductivity.[7,8]

Polarized Cu L_3 x-ray-absorption spectroscopy (XAS) is a unique tool to determine the symmetry of the unoccupied Cu $3d$ states at the Cu site. Several polarized Cu L_3-XAS measurements have led to the conclusion that the unoccupied Cu $3d$ states mainly have $3d_{x^2-y^2}$ character with 10–20 % weight of Cu $3d_{z^2-r^2}$ character.[11–19] Most of these reports also detect an energy shift of about 200–500 meV between the $E\|(a,b)$ and $E\|c$ polarized spectra.[12,15,18,20] Except for a few,[17] the majority of studies reporting relatively high weight of Cu $3d_{z^2-r^2}$ and an energy shift between white lines of different polarizations used a surface sensitive total yield (TY) as the mode of detection.[12,15,16,18,20] On the other hand, studies using bulk sensitive fluorescence yield (FY) mode of detection and electron energy loss spectroscopy (EELS) showed less weight for the out-of-plane Cu $3d_{z^2-r^2}$ states and no or negligible energy shift between the $E\|(a,b)$ and $E\|c$ polarized spectra.[11,13,14,19,21–23]

In the XAS studies on nearly optimally doped Tl(2212) and Tl(2223) thin films and single crystals,[11–14] the fraction of holes with $3d_{z^2-r^2}$ character has been reported to be 10–12 % to the total number of Cu $3d$ holes. It is suggested that this amount is an admixture of $3d_{z^2-r^2}$ states in the in-plane Cu $3d$–O $2p_{x,y}$ band. The band structure calculations have also predicted an admixture of about 10% Cu $3d_{z^2-r^2}$ states to the Cu $3d_{x^2-y^2}$–O $2p_{x,y}$ band.[24] However, recent studies[22,23] reporting the absence of Cu $3d_{z^2-r^2}$ states in Bi(2212) system put a question mark on the above fact.

Different interpretations have been given to explain the observed energy shift between the $E\|(a,b)$ and $E\|c$ spectra. An existence of a narrow band having $3d_{z^2-r^2}$ character at E_f was suggested in order to explain the same.[25] Also, correlations were obtained between T_c and the energy difference (Δz) between the $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ lines.[20] It has also been argued that this shift may be a surface artifact and therefore may be due to the detection mode used.[21] The shift has also been explained by taking into account angular resolved photoemission and O K-edge measurements.[20] Efforts have been made to settle down the existing discrepancies regarding the shift;[25] however, until now, comparison has been made either between the data reported by different groups on different samples of the same or different stoichiometry or using the data collected by different detection modes or techniques.

In our recent work,[26] we have highlighted the importance of using a bulk sensitive detection mode and a precise knowledge of sample stoichiometry in order to arrive to a reliable estimation of out-of-plane Cu $3d_{z^2-r^2}$ states in Tl

bilayer cuprates. We had shown using overdoped Tl(2212) thin films, that the sample treatment conditions can lead to an appreciable amount of holes having Cu $3d_{z^2-r^2}$ character without affecting the T_c to a great extent. Our results indicated that doping induces Cu $3d_{z^2-r^2}$ orbitals to mix with an O $2p$ valence band corresponding to a $|3d_{z^2-r^2}\underline{L}\rangle$ configuration. It was also shown that the presence of a high amount of holes having Cu $3d_{z^2-r^2}$ symmetry was neither beneficial nor detrimental for superconductivity and theories based on the large fraction of these out-of-plane states were ruled out.

In the present work, we have attempted to understand the role of out-of-plane Cu orbitals in Tl bilayer cuprates. The Cu L_3 measurements, on well characterized Tl(2212) thin films, synthesized in different conditions, using a bulk sensitive FY detection mode are presented. Thereafter, we have commented on the observed energy shift in the energy position of the white lines in $E\|(a,b)$ and $E\|c$ polarizations by making a comparison between well characterized TI(2212) thin films with different amount of dopings.

II. EXPERIMENT

The thin films were deposited on $LaAlO_3$ (100) oriented by multitarget sputtering. Two cathodes were fitted with insulating targets of $Ba_{1.8}Ca_{0.2}CuO_3$ and Ca_2CuO_3 and were rf biased. Two other cathodes were fitted with metallic targets (TI and Cu) and were dc biased. The deposition time was 12 h in order to obtain 3000 Å thickness. As-deposited films were insulating and amorphous. Two types of annealing treatments were performed on these films. The first film was annealed in a sealed tube under low oxygen pressure (1 bar of oxygen) and hereafter will be mentioned as vacuum synthesized in the text. The second film was annealed in a sealed tube under medium oxygen pressure (10 bars of oxygen). 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 indicate T_c of 105 K for the first thin film and 100 K for the second one as shown in Fig. 1.

The Cu L_3-edge spectra have been recorded at room temperature in fluorescence yield mode on the SA32 line of the SUPER ACO facility (LURE, Orsay) operating at 800 MeV and 200 mA. The x rays were monochromatized by two beryl crystals ($10\bar{1}0$). The energy scale was then set with respect to the $|3d^9\rangle$ peak of CuO at 931.2 eV. The experimental energy resolution was estimated to be better than 0.3 eV, whereas the reproducibility of the energy position is close to 0.05 eV. The width of the core hole has been measured to be equal to 0.56 eV at the L_3 edge. For the detection, a seven Ge diodes detector was used with an axis at 45° from the beam axis.

A standard procedure has been adopted to remove the background contribution, and the normalization point was chosen on the continuum at 948 eV. The relative intensity of both the lines $3d^9$ and $3d^9\underline{L}$ have been determined by simulating the spectra with a combination of Gaussian and Lorentzian shapes using a program written by Rodriguez to fit neutron diffraction line profiles. The initial program was modified to take into account the specifities of x-ray absorption data and to introduce linewidth per peak as a fitted

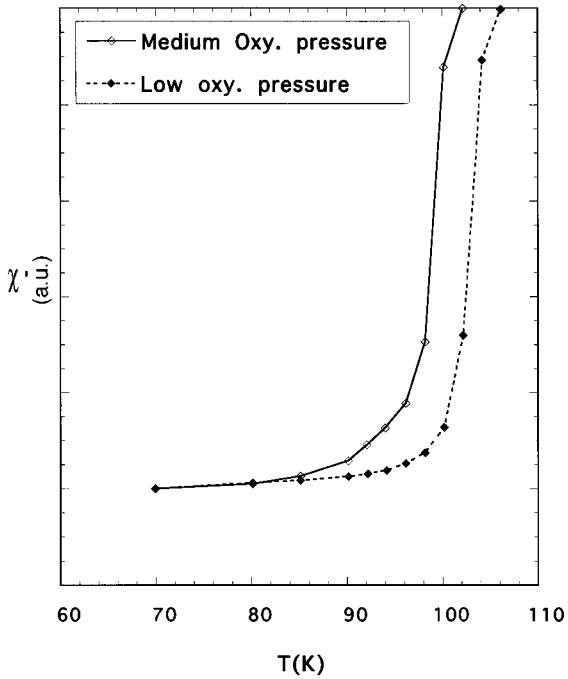

FIG. 1. ac susceptibility $\chi'(T)$ for the low and medium oxygen pressure annealed thin films.

parameter.[27] The density of doping holes was calculated through the relation

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

III. RESULTS AND DISCUSSION

A. Role of out-of-plane Cu orbitals

The Cu L_3-edge spectra of Tl(2212) thin films have been recorded at room temperature using bulk sensitive fluorescence yield (FY) mode. The spectra obtained using the FY mode were corrected following the work of Tröger *et al.*[28] which describes a full correction method of the self-absorption in soft fluorescence extended x-ray fine structure. As shown in our recent work,[26] the correction enhances the white line $|3d^9\rangle$ intensity with respect to the $|3d^9\underline{L}$ one and decreases the $|3d^9\rangle$ linewidth with respect to the total yield spectrum. The spectra of the two Tl(2212) thin films synthesized in vacuum and under medium oxygen pressure at different orientations obtained after the correction are shown in Figs. 2 and 3, respectively. As can be seen from Figs. 2 and 3, the intensity of the $|3d^9\rangle$ peak decreases as the angle of incident electric field increases with respect to the film surface. In order to obtain covalent and doping hole densities, the spectra were least squares fitted. Using a dipolar angular variation of the form $I_{|3d^9\rangle}(0°)\cos^2\theta + I_{|3d^9\rangle}(90°)\sin^2\theta$, the intensity can be extrapolated to $\theta = 90°$. For the vacuum synthesized thin film, the density of covalent holes along the z axis was estimated to be ≈10%. However, no $|3d^9\underline{L}\rangle$ doping holes were found to have z symmetry [Figs. 4(a) and 4(b)]. On the other hand, the thin film synthesized in medium pressure of oxygen (10 bars) gives 12% and ≈2% covalent and doping hole densities along the z axis, respectively [Figs. 5(a) and 5(b)]. The density of doping holes per Cu (n_h) and total density of holes ($3d^9 + 3d^9\underline{L}$), taking the intensity of

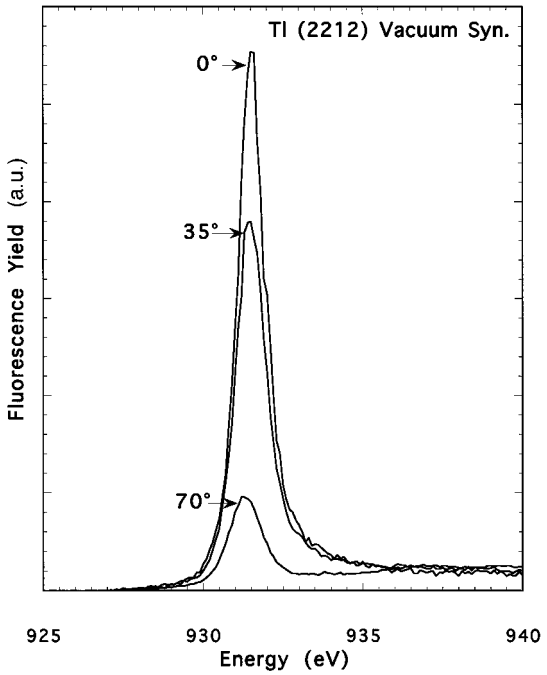

FIG. 2. Cu L_3-edge spectra of the Tl(2212) thin film synthesized in low pressure of oxygen (1 bar) measured at different orientations with respect to the (a,b) plane by the fluorescence yield detection mode.

$3d^9$ white line in $E\|(a,b)$ polarization as 100%, for both thin films, are listed in Table I. The estimated density of covalent and doping holes along the z axis for the vacuum synthesized film is in agreement with our previous study.[12] However, the total $(3d^9+3d^9\underline{L})$ density of holes in out-of-plane hole Cu orbitals in the case of Tl(2212) thin film synthesized under medium pressure of oxygen turns out to be 14%, which is 5% more with respect to the vacuum synthesized Tl(2212) thin film (see Table I). The T_c decreases from 105 to 100 K, which as we have conclusively proved in our previous work[12,29] is due to the change in density of in-plane doping holes which changes from 0.15 to 0.20 in the two films synthesized in vacuum and medium oxygen pressure. As can be seen, the value of n_h in both Tl(2212) thin films is more than the optimum value ($\approx$0.12) obtained in our previ-

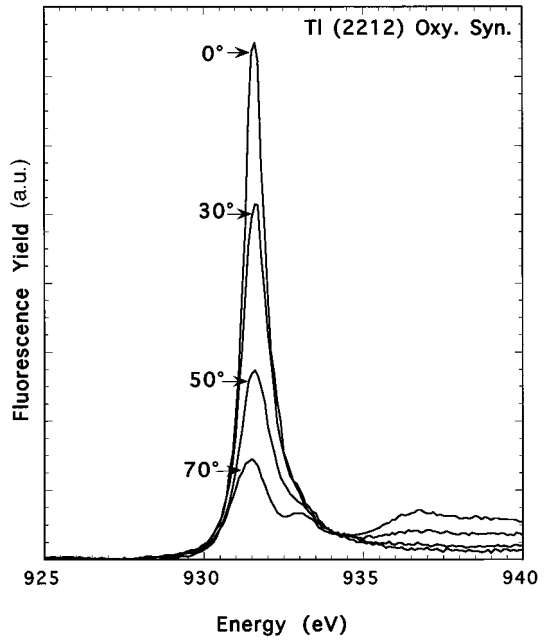

FIG. 3. Cu L_3-edge spectra of the Tl(2212) thin film synthesized in medium pressure of oxygen (10 bar) measured at different orientations with respect to the (a,b) plane by the fluorescence yield detection mode.

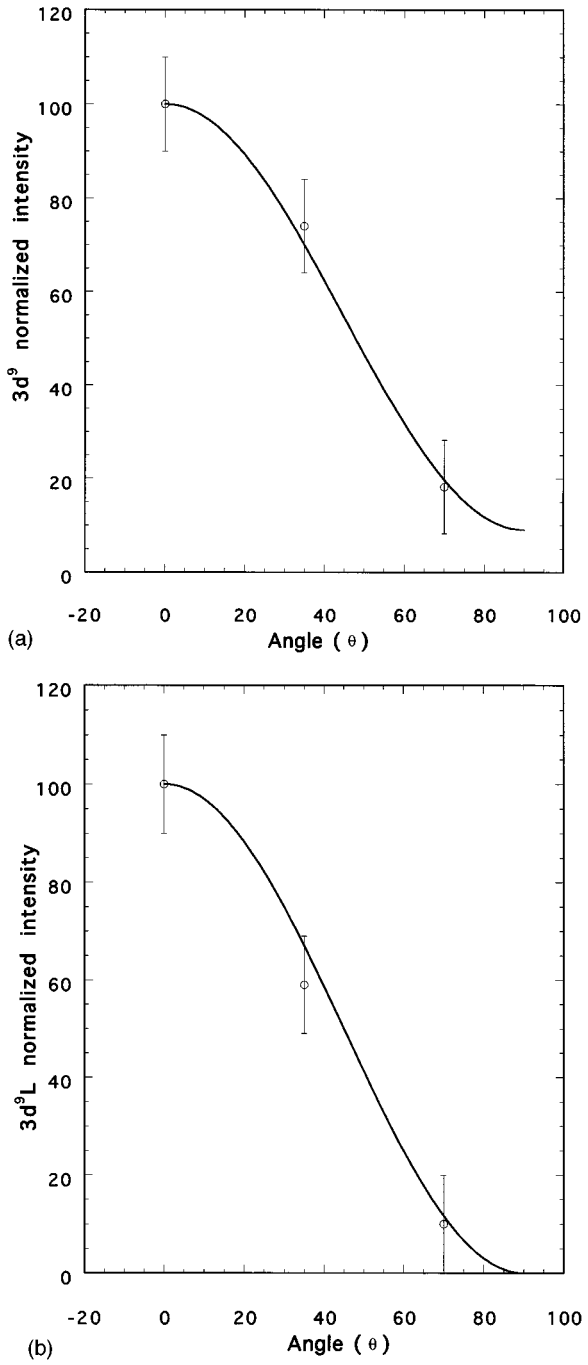

FIG. 4. Variations of the total (a) $3d^9$ and (b) $3d^9\underline{L}$ normalized intensities versus the angle between incident electrical field and the (a,b) plane of Tl(2212) structure using the fluorescence yield detection mode. A fit by a dipolar law of the type $I(\theta)=I(0°)\cos^2(\theta)+I(90°)\sin^2(\theta)$ allows an extrapolation to 90° to be performed.

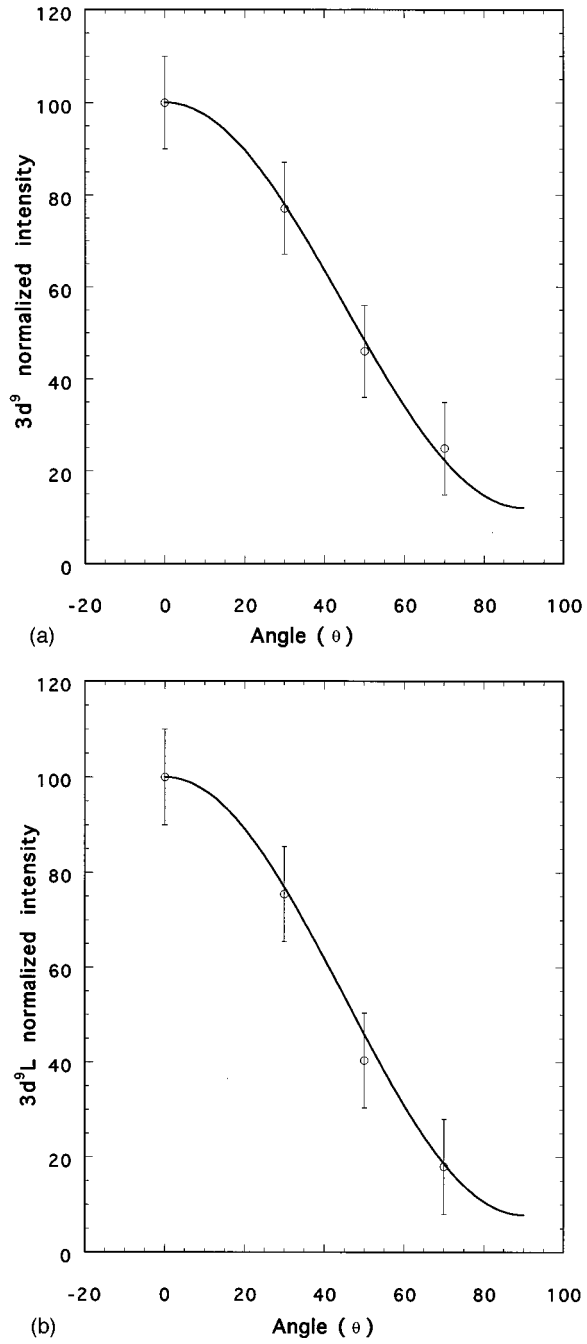

FIG. 5. Variations of the total (a) $3d^9$ and (b) $3d^9\underline{L}$ normalized intensities versus the angle between incident electrical field and the (a,b) plane of Tl(2212) structure using the fluorescence yield detection mode. A fit by a dipolar law of the type $I(\theta)=I(0°)\cos^2(\theta)+I(90°)\sin^2(\theta)$ allows an extrapolation to 90° to be performed.

ous study[12,29] which resulted in the value of T_c which is less than the highest observed in this system. We have already shown an even higher amount of density of holes having $3d_{z^2-r^2}$ character in the Tl(2212) thin film synthesized under high (70 bars) oxygen pressure, again without any appreciable change in T_c.[26] These observations compels one to think that the Cu $3d_{z^2-r^2}$ orbitals essentially act as the hole reservoirs.

On overdoping, the asymmetry of crystal field is reduced by the change in local environment of Cu. Previous works have shown as a general trend that the c unit cell parameter in thallium bilayer cuprates decrease under doping and vice versa indicating a consequent decrease of the Cu-O apical distance.[30] This reduces the splitting between $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ states, pushing the Cu $3d_{z^2-r^2}$ states closer to the E_f, leading to an increasing number of holes on Cu $3d_{z^2-r^2}$ orbitals. This implies that at high doping a band of $3d_{z^2-r^2}$ character starts emerging at the E_f. This $3d_{z^2-r^2}$ orbital mixes with the O $2p$ valence band which is indicated by the presence of doping hole density along the z axis in the Tl(2212) thin film synthesized under medium pressure of oxygen, corresponding to an expected $|3d^9{}_{z^2-r^2}\underline{L}\rangle$ configuration. Hence, after a certain amount of doping, exchange does take place between Cu and its apical oxygens and as suggested by our recent O K and Tl L_3-edge measurements,[26,31] a higher amount of doping holes could be stabilized in the Tl-O layers via these apical oxygens.

However, the presence of a high density of holes having Cu $3d_{z^2-r^2}$ character does not seem to play an active role in the mechanism of superconductivity as the small decrease in T_c can be explained in terms of the variation in density of doping holes having in-plane symmetry. These results are in agreement with the study of Pellegrin *et al.*,[13] which has concluded no direct correlation between Cu $3d_{z^2-r^2}$ and T_c in Tl bilayer and three layer superconductors though their study was restricted to only one doping hole concentration.

The fraction of holes with $3d_{z^2-r^2}$ character as compared to the total number of Cu $3d$ holes (both in plane and out of plane) turns out to be ≈8% and ≈10% for the vacuum and oxygen synthesized thin films, respectively (see Table II). Both these values are quite close to the one reported by Romberg *et al.*,[11] which reported ≈10% density of holes having Cu $3d_{z^2-r^2}$ character in Tl(2212) single crystal having a T_c of 101 K using EELS technique. This result has important implications in the present work which would be made clear in the next section. These values also agree well with the amount of Cu $3d_{z^2-r^2}$ character (≈10%) which is suggested to be admixed with the in-plane Cu $3d_{x^2-y^2}$–O $2p_{x,y}$ band by band structure calculations.[24] The presence of 10–12 % Cu $3d_{z^2-r^2}$ holes in nearly optimally doped Tl cuprates needs to be examined carefully. Whether this is the fraction of Cu $3d_{z^2-r^2}$ holes admixed with Cu $3d_{x^2-y^2}$–O $2p_{x,y}$ band or a critical fraction which is compatible with the total number of doped holes as pointed out by Feiner *et al.*[32] is still a debatable question. However, recent reports[22,23] suggesting complete absence of Cu out-of-plane orbitals emphasize the difference between Bi and Tl bilayer cuprates. This difference is reflected in the degree of anisotropy as observed by electrical and magnetic measurements on these compounds. More extensive angle-resolved photoemission spectroscopic studies on well characterized thin films and single crystals as a function of doping would help in solving this problem.

The strongly polarization dependent steplike structures for $E\|c$ at 937 eV have already been observed in several studies of Bi2212 (Ref. 33) and Tl2212 (Refs. 13 and 34) compounds. Although the debate on the origin of these broad maxima is still running, two main hypotheses have been con-

TABLE I. Comparison between density of covalent and doping holes in the two Tl(2212) thin films synthesized in low (1 bar) and medium (10 bar) oxygen pressures. The $3d^9$ and $3d^9\underline{L}$ contributions are calculated taking intensity of the white line $|3d9\rangle$ in the (a,b) plane as 100%. θ is the angle between electric field E and (a,b) plane and n_h represents density of doping holes per copper.

Sample	T_c	θ	$3d^9$	$3d^9\underline{L}$	n_h
Tl(2212)	105 K	0°	100	18.1	0.153
		35°	74.1	10.6	0.125
		70°	18.2	1.8	0.09
		90°[a]	10.0[a]	0[a]	0[a]
Tl(2212)	100 K	0°	100	24.8	0.20
		30°	77.1	18.7	0.195
		50°	46.0	10.0	0.177
		70°	25.0	4.5	0.152
		90°[a]	12.0[a]	2.0[a]	0.143[a]

[a]Obtained by extrapolation.

sidered since the beginning: either (i) a mixing of Cu $3d_{z^2-r^2}$, Cu $4s$, and apical O $2p_z$ orbitals or (ii) hybridization of Cu $3d_{z^2-r^2}$ and Cu $4p_z$ of adjacent $[CuO_2]$ layers. Indeed Pellegrin *et al.* have shown that the second hypothesis must be ruled out since this feature is also present for $E\|c$ in single copper layer high-T_c superconductors. The first hypothesis, which corresponds to itinerant holes delocalized along the c axis, is more in agreement with the observations of this paper. A strong increase of that feature at 937 eV is observed between the thin film synthesized under low oxygen pressure (1 bar) (Fig. 2) and the one synthesized under medium oxygen pressure (10 bars) (Fig. 3). Thus it appears that the electronic levels giving rise to this feature might also play the role of hole reservoir concurrently with the direct hybridization between Cu $3d_{z^2-r^2}$ and O $2p_z$ orbitals as described above. The Cu L_3-edge spectra of the thin film synthesized under high oxygen pressure (70 bars) will be presented soon in another paper dealing with the existence of out-of-plane hole density in layered superconductors. They showed also the existence of a strong feature at 937 eV for $E\|c$ but with an intensity similar to the one of the medium pressure synthesized film: indeed, in that case, doping holes are created more in the $|3d^9{}_{z^2-r^2}\underline{L}_z\rangle$ configuration than in the Cu $3d_{z^2-r^2}$–Cu $4s$–O $2p_z$ orbitals as shown in Table II.

B. Energy splitting (Δz) of in-plane and out-of-plane polarized spectra

To find a probable explanation for the observed energy shift between the energy positions of white lines of in-plane $[E\|(a,b)]$ and out-of-plane $(E\|c)$ polarized spectra, we present our observations on well characterized Tl(2212) thin films synthesized in different conditions. Various parameters of different thin films are summarized in Table II. All results listed in the table are obtained using the bulk sensitive fluorescence yield (FY) detection mode, and are confined to only Tl(2212) to avoid complications in the interpretation of results. As evident from Table II, we do observe an energy splitting (Δz) between in-plane and out-of-plane polarized spectra and the splitting decreases with increasing amount of doping. The existence of an energy splitting using a bulk sensitive FY mode is in contradiction with the previous studies reporting no splitting in various high-T_c superconductors using FY and EELS techniques.[11,13,14,19,21] This probably can

TABLE II. Energy splitting (Δz) between white lines $|3d^9\rangle$ in $E\|(a,b)$ and $E\|c$ polarizations and fraction of holes in out-of-plane Cu orbitals $(3d_{z^2-r^2})$ as compared to the total density of holes $(3d_{\text{total}}$, including both covalent and doping density of holes in and out of plane) in Tl(2212) thin films synthesized in different conditions.

Sample	Synthesis conditions	T_c	Δz	$3d_{z^2-r^2}/3d_{\text{total}}$
Tl(2212) thin film	In low (1 bar) oxygen pressure	105 K	210 meV	8.0%
Tl(2212)[a] thin film	In high (70 bar) oxygen pressure and post-annealed in Ar	105 K	200 meV	9.5%
Tl(2212)[a] thin film	In medium (10 bar) oxygen pressure	100 K	135 meV	10%
Tl(2212)[a] thin film	In high (70 bar) oxygen pressure	100 K	100 meV	18%

[a]For details see Ref. 26.

be understood by looking at the characteristic data of different samples showing no shift between the energy positions of in-plane and out-of-plane white lines, e.g., the Tl(2212) single crystal used by Romberg *et al.*[11] was showing a T_c of 101 K and the value of Δz was reported to be zero (<50 meV). Referring to Table II, we find that value of T_c of the single crystal used by Romberg *et al.* is quite close to our thin films synthesized under medium pressure (10 bars of oxygen) and high pressure (70 bars of oxygen) which show $\Delta z \approx 100-135$ meV. This implies that probably the single crystal was overdoped which resulted in the low value of Δz. Bianconi *et al.*[25] have also found the energy splitting (Δz) to be doping dependent in Bi cuprates. They have also suggested that the difference in the estimation of energy splitting (Δz) is not due to the different techniques used but the intensity and energy position of polarized white lines change with the type of dopants and not with doping as different dopants can induce different distortions at the Cu site. Conversely, in the present case, it is quite clear that the energy splitting (Δz) is doping dependent as we have put different amounts of oxygen in Tl(2212). Whether the splitting changes with different types of dopants is still questionable.

The probable reason for the presence of an energy splitting (Δz) between the in-plane and out-of-plane polarizations and its variation with doping can be understood by taking into account the observed presence of a small amount ($\approx 10\%$) of unoccupied $3d_{z^2-r^2}$ states in the ground state of nearly optimally doped Tl(2212) and the increase in the fraction of states having Cu $3d_{z^2-r^2}$ character at the E_f on doping. The energy splitting (Δz) then can be taken as the measure of energy difference between in-plane and out-of-plane states, i.e., states having different symmetries, and hence related with the Jahn-Teller splitting. On doping, the extra oxygen holes change the environment around Cu resulting in the reduction of asymmetry of crystal field and thereby reducing the splitting between $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ states. This results in the observed reduction in the energy splitting (Δz) between out-of-plane and in-plane polarized white lines. This explanation seems to work well with the Tl bilayer cuprates, as to the best of our knowledge, XAS studies reported so far on these compounds have estimated a presence of 10–12 % density of holes having $3d_{z^2-r^2}$ symmetry. Recent reports[22,23] showing complete absence of these states in Bi(2212) system may probably be due to variation in the energy of $3d_{z^2-r^2}$ states in Bi(2212) as compared to Tl(2212). It appears, due to the difference in crystal field splitting, the difference between the energies of $d_{x^2-y^2}$ and d_{z^2} states is more in Bi cuprates as compared to Tl cuprates. In Bi cuprates the d_{z^2} states lie below the E_f and remain occupied at least on optimal amount of doping resulting into the absence of unoccupied $3d_{z^2-r^2}$ states.

Contrary to the findings of Bianconi *et al.*,[20] no correlation was found between T_c and the energy splitting (Δz). In the present case the fraction of total $3d_{z^2-r^2}$ character as compared to the total number of Cu $3d$ holes increases with doping (see Table II). The slight variation in the values of T_c is not due to this increase in $3d_{z^2-r^2}$ character but is related to the variation of in-plane density of doping holes as pointed out in the previous and present studies. This once again emphasizes the fact that out-of-plane Cu orbitals play the role of hole reservoir. Also, no correlation between T_c and the energy splitting (Δz) rules out theories such as, e.g., the d-d excitation model[5,6] which predicts increase of T_c with increasing weight of $3d_{z^2-r^2}$ component and decreasing energy splitting between the $d_{x^2-y^2}$ and $d_{z^2-r^2}$ states.

IV. CONCLUSIONS

We have studied the role of Cu out-of-plane orbitals in the Tl(2212) superconductor. Our results suggest that these orbitals essentially play a role of hole reservoir at least in Tl(2212). Contrary to the recent XAS studies on Bi(2212) and in agreement with the ones reported so far on Tl cuprates, we have found a small fraction ($\approx 10-18$ %) of Cu $3d_{z^2-r^2}$ states as compared to the total $3d$ holes, depending on the amount of doping. Whether this fraction is an admixture of $3d_{z^2-r^2}$ states in the in-plane Cu $d_{x^2-y^2}$–O $2p_{x,y}$ band and hence should always be present or a critical amount which should be compatible with the amount of doping is still not clear. The energy splitting between the white lines of in-plane [$E\|(a,b)$] and out-of-plane ($E\|c$) polarizations was found to be doping dependent and a probable explanation has been given for the observed splitting.

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