Role of Out-of-Plane Copper and Thallium Orbitals in Thallium Cuprate

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Abstract. Simultaneous total and fluorescence yield XAS measurements on Cu L_3-edge and, for the first time, total yield measurements at Tl L_3-edge of well oriented Tl(2212) thin films are reported in this work. Also, Cu L_3 and O K-edge measurements on overdoped Tl(2212) thin films using bulk sensitive fluorescence yield detection mode are reported showing that large out-of-plane hole densities do exist in the thallium cuprates at least for overdoped samples. Our results suggest that use of a bulk sensitive technique is necessary in order to get a reliable estimation of states having Cu $3d_{z^2-r^2}$ character and thus a precise knowledge of sample stoichiometry. No direct correlation is found between Tc and out-of-plane covalent and doping hole densities such that theories based on the existence of large fraction of these out-of-plane unoccupied states are ruled out. To understand the role of out-of-plane copper orbitals, polarization dependent measurements of Cu L_3-absorption edge on well characterised 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.

1.INTRODUCTION

The Bi (2212) and Tl (2212) have notable differences in their electronic structure and superconducting properties inspite of having a similar crystal structure with three types of oxygen atoms located in CuO2 [O(1)], Sr(Ba)O [O(2)] and Bi(Tl)O [O(3)] layers. In Tl (2212), out-of-plane bond lengths of Tl-O(2) and Tl-O(3) are shorter than the in-plane bond lengths of Tl-O(3) [1,2]. This makes charge transfer and interlayer coupling quite probable [3,4]. However, till now Tl-cuprates are not as extensively studied as the Bi-cuprates because of complexities involved in the preparation of high quality thallium thin films and single crystals. In our previous contribution [5], we have reported polarized Cu L_3 measurements on well oriented Tl(2212) thin film in order to study symmetry and density of doping holes and their influence on Tc. The doping holes were found to have only in-plane symmetry. A previous comparison between TY and FY detection modes Cu L_3-edges of Tl(2212) thin films has shown no differences in the E//(a,b) spectra (normal incidence) after full correction for the self reabsorption efeects in FY mode but significant difference in the E//c-axis (grazing incidence) due to surface effects.

In the present contribution, using the FY detection mode polarized Cu L_3 measurements on three different Tl (2212) thin films synthesized and annealed in different conditions and O K-edge measurement on one thin film are presented. These measurements were performed at two different beamlines. Using these, the existence and role of doping hole density in the out-of-plane orbitals is discussed in Tl bilayer cuprates.

2.EXPERIMENTAL

The thin films were deposited on $LaAlO_3$ (100) oriented by multitarget sputtering. The details of the deposition process is described elsewhere [6]. 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 Tc of 105K for the post annealed thin film and 101K for the remaining two.

The Cu L_3-edge spectra have been recorded at room temperature both in the Total and Fluorescence Yield modes on the SA32 line of the SUPER ACO facility (LURE, Orsay) operating at 800 MeV and 200 mA. The XAS measurements for one of the thin films were performed at AT&T Bell Labs, Dragon beamline at NSLS, Brookhaven National Lab. A standard procedure has been adopted to remove the background contribution, and the normalization point was chosen on the continuum at 948 eV.

3. RESULTS AND DISCUSSION

3.1. Cu L_3-EDGE

3.1.1. Existence of doping hole density in out-of-plane Cu orbitals

Cu L_3 spectra measured on a high oxygen pressure (70 bars) annealed Tl(2212) thin film is shown in figure 1. The spectra were recorded on the Dragon beamline at BNL. The appreciable amount of the $3d^9\underline{L}$ peak at 75°is very much evident, clearly depicting the existence of out-of-plane doping holes. After full correction for the self-absorption in soft fluorescence extended X-ray fine structure, the spectra were then simulated and using the dipolar angular variation form density of covalent and doping holes along the z-axis were estimated. The covalent and doping hole density along the z-axis are 25% and 15% respectively. This is quite an appreciable amount in comparison to the thin film synthesized under low oxygen pressure (Fig.2) which shows 10% and 0% covalent and doping holes along the z-axis. However the Tc increases only from 100K to 105K from the former to the latter. This implies that, after a certain amount of doping, exchange do take place between Cu and its apical oxygens, leading one to assume that $3d_{z^2-r^2}$ orbital mixes with O 2p valence band. The probable explanation of detection of

doping holes having $3d_{z^2-r^2}$ symmetry in these overdoped Tl (2212) thin films can be derived from the fact that the extra oxygen holes change the environment around Cu resulting in the reduction of asymmetry of crystal field. This in turn reduces the splitting between $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ states, pushing the $3d_{z^2-r^2}$ states closer to the E_f leading to an increasing number of holes on $3d_{z^2-r^2}$ orbitals.

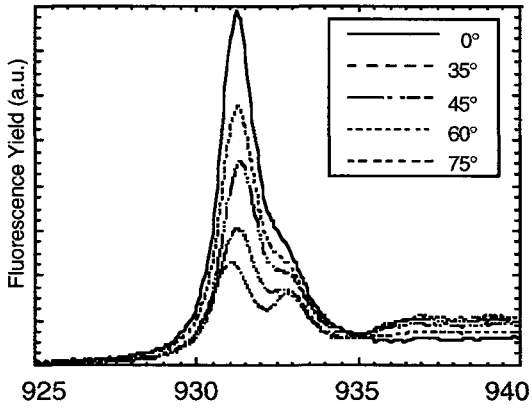

Fig.1: Polarized FY Cu L_3-edges of a Tl(2212) thin film synthesized under high oxygen pressure (70 bars).

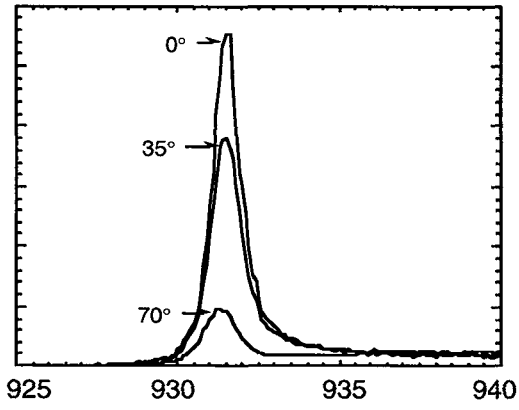

Fig.2: Polarized FY Cu L_3-edges of a Tl(2212) thin film synthesized under low oxygen pressure (1 bar).

The slight decrease in Tc observed in the overdoped sample is related to the variation in the in-plane density of holes crossing the optimum value [5,6] and is not due to the observed increase in amount of holes having Cu $3d_{z^2-r^2}$ symmetry. This clearly implies that these states are neither beneficial nor detrimental to the cause of superconductivity as concluded by Pellegrin et al [7] for bi-layer and three layer Tl-cuprates.

3.1.2. Role of out-of-plane copper 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 [8] which describes a full correction method of the self-absorption in soft flurorescence extended x-ray fine structure. The correction enhances the white line $|3d^9\rangle$ intensity with respect to the $|3d^9\underline{L}\rangle$ one and decreases the $|3d^9\rangle$ line width 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 figures 2 and 3 respectively. 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. On the other hand the thin film synthesised in medium pressure of oxygen (10 bars) gives 12% and ≈2% covalent and doping hole densities along the z-axis respectively. The total $(3d^9+3d^9\underline{L})$ density of holes in out-of-plane 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. The T_C decreases from 105K to 100K, which as we have conclusively proved in our previous work [5,9] is due to the change in density of in-plane doping holes which changes from 0.15 to 0.20 in the two films synthesised 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 (≈0.12) obtained in our previous study [9,10] which resulted in the value of Tc which is less than the highest observed in this system. 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 [10]. 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. These $3d_{z^2-r^2}$ orbital mixes with 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 do take place between Cu and its apical oxygens and as suggested by our recent OK and Tl L_3-edge measurements [11], higher amount of doping holes could be stabilized in the Tl-O layers via these apical oxygens.

However, the presence of 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 Tc 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 [7], which leads to the conclusion that no direct correlation exists between Cu $3d_{z^2-r^2}$ and T_C in Tl bi-layer and three layer superconductors though their study was restricted to only one doping hole concentration.

3.2. O K- AND Tl L_3-EDGES

Figure 4 shows polarized OK-edge spectra using bulk sensitive FY mode at different orientations on the same thin film synthesized under high oxygen pressure as in figure 1. The E//(a,b) and E//c measurements probe unoccupied states with O $2p_{x,y}$ and O $2p_z$ characters respectively.

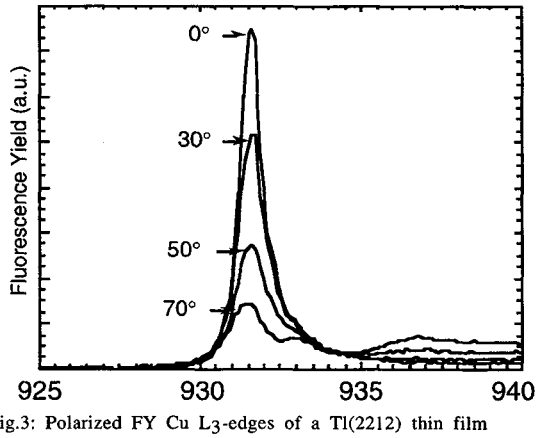

Fig.3: Polarized FY Cu L_3-edges of a Tl(2212) thin film synthesized under medium oxygen pressure (10 bars).

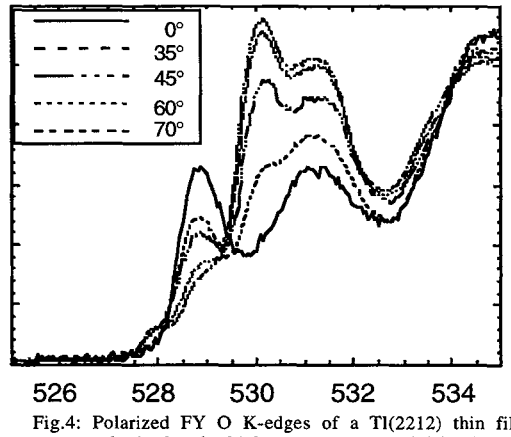

Fig.4: Polarized FY O K-edges of a Tl(2212) thin film synthesized under high oxygen pressure (70 bars).

The E//a,b spectrum consists of two features, a prepeak at 528.4 and a broad feature around 530.7 eV. The prepeak in E//(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 $|3d^9\underline{L}>$ representation and referred to ligand band in the effective one-band Hubbard model [10] extended to O K-edge. We have estimated its intensity for the 90° (E//c) incidence spectrum and found it to be negligible within the experimental error. This confirms that the doping holes have predominantly O $2p_{x,y}$ symmetry .

Changing the polarization from E//(a,b) to E//c, the intensity of the prepeak at 528.4 decreases drastically and another peak and a broad structure appear around 529.7 and 530.8 eV respectively. Taking into consideration the chemical shifts calculated by band structure calculations [4,12] for Tl-cuprates, the features observed at 529.7 and 530.8 eV in the spectrum recorded at 80° incidence are ascribed to O(2) and O(3) 2p states respectively. According to the 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 at the Fermi level consist of O(2)-Tl-O(3) band formed by the hybridization of Tl 6s and Tl $5d3_z{}^2{}_{-r}{}^2$ orbitals and O(2) and O(3) $2p_z$ orbitals and therefore have predominantly O $2p_z$ character. The hybridization is quite strong due to relatively short distances between Tl and apical O atoms (Tl-O(2) = 2.05 Å and Tl-O(3) = 2.42 Å). Here we would like to point out that the intensity of the feature at 530.8 eV, corresponding to the Tl-O(3) bond, is high, specially on the spectrum recorded at 80° incidence (Figure 8), as compared to the ones reported on under or optimally doped Tl(2212) thin films and single crystals [7]. This suggests that extra oxygens could be stabilized in the Tl-O layers in these synthesis conditions under high oxygen pressure.

The origin of the broad structure at 530.7 eV in E//a,b spectrum is still not clear. As suggested by Pellegrin et al [7] 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 O(2) and/or O(3) atoms. From our spectrum it appears that contribution from O(3) states is more than the O(2) states. Also, polarized XAS experiments at Tl L_3-edge on the same thin films have shown that, due to the short Tl-O(2) distances, a strong charge tranfer takes place from the O(2) apical oxygen and, to a smaller extent, from the O(3) oxygen to the Tl along the c-axis. This is in agreement to our earlier studies [1] and also with band structure calculations for this system [11] which predict that the electron pockets at E_f are formed from an antibonding band composed of O(2) $2p_z$ and O(3) $2p_z$ orbitals hybridized with Tl 6s and Tl $5d3_z{}^2{}_{-r}{}^2$ orbitals.

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