CHAPTER 6

THALLIUM L - ABSORPTION EDGE STRUCTURE
6.1 INTRODUCTION

It is well known\textsuperscript{1-5} that monovalent and trivalent thallium compounds have interesting chemistry as a consequence of \textsuperscript{6}s and \textsuperscript{6}p electrons present in the valence band. The nature of the bonding in these compounds also varies widely. For example, covalent contributions to the bondings\textsuperscript{6} in thallium (I) halides reach a maximum with TlI which has a double-layered orthorhombic structure\textsuperscript{7}.

A feature of fundamental importance which influences the structure and bonding in Tl compounds is that the \textsuperscript{6}s, \textsuperscript{6}p and \textsuperscript{6}d levels are sufficiently close and hybridization of these orbitals is energetically favourable in several Tl compounds. Hybridization alters the character of the otherwise pure and vacant \textsuperscript{6}p and \textsuperscript{6}d levels of monovalent and trivalent thallium in covalently bonded compounds. In the absence of hybridization, like in ionically bonded Tl\textsuperscript{1+} or Tl\textsuperscript{3+} compounds, the same \textsuperscript{6}p and \textsuperscript{6}d levels are subject to strong crystal field effects of the coordination sphere of ligands and depending on the point group symmetry of the thallium atom, degeneracies of the p and d manifolds are lifted up. Hence it suggests that in either situation, XANES spectroscopy should prove to be a very strong informative experimental approach to study the coordination geometry and bonding relations in thallium compounds. Since the near-edge features involve the transition from some core states to allowed lowest unoccupied empty states in the valence region of a given atomic centre, XANES spectra should reveal not only the allowedness or otherwise of these transitions but also the mixing or splitting of the final state orbitals\textsuperscript{8-9}. In this Chapter, we report XANES and EXAFS investigations of selected monovalent and trivalent thallium compounds where using the known structural data, informative deductions on structural-bonding relations have been made. Both Tl \textsubscript{L\textsuperscript{II,III}} and \textsubscript{L\textsuperscript{I}} edge XANES spectra have been used since they probe \textsuperscript{2}s ---\textsuperscript{6}p and \textsuperscript{2}p ---\textsuperscript{6}d transitions.
transitions respectively.

Also since X-ray spectra probe dominantly the effect of local coordinations, we have extended the investigations to a new class of superconducting oxides containing thallium\textsuperscript{10-14}, which show the highest transition temperatures to-date. We may expect on reasonable grounds that the near-edge analysis of these superconductors will provide us the information on atomic environment of thallium ions.

In previous Chapter, we have studied V K-edges in CrVO\textsubscript{4}, GdVO\textsubscript{4}, BiVO\textsubscript{4}, Cd\textsubscript{2}V\textsubscript{2}O\textsubscript{7}, Ca\textsubscript{3}Fe\textsubscript{3}GeVO\textsubscript{12}, Pb\textsubscript{5}(VO\textsubscript{4})\textsubscript{3}Cl, Zn\textsubscript{3}(VO\textsubscript{4})\textsubscript{2}, NaVO\textsubscript{3}, VO(acac)\textsubscript{2}, (NH\textsubscript{4})\textsubscript{4}[VO-dd-tart].\textsubscript{2}2H\textsubscript{2}O, VOPc, VO(bzac)\textsubscript{2}, VOTPP, VOMoO\textsubscript{4}, V\textsubscript{2}O\textsubscript{5}, VO, (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}.VS\textsubscript{4}.6H\textsubscript{2}O, V\textsubscript{2}O\textsubscript{3}, SmVO\textsubscript{3}, V\textsubscript{2}S\textsubscript{3}, VN, VO\textsubscript{2}, V\textsubscript{4}O\textsubscript{7}, VC, [VO(hshd)(acac)], PbV\textsubscript{2}O\textsubscript{6}, Ca\textsubscript{3}V\textsubscript{10}O\textsubscript{28}.16H\textsubscript{2}O.

and the superconducting cuprate oxides of composition Tl\textsubscript{1-x}V\textsubscript{x}Sr\textsubscript{2}(Ca\textsubscript{0.8}Y\textsubscript{0.2})Cu\textsubscript{2}O\textsubscript{y}, where x = 0.2, 0.3, 0.4 and 0.5. Our XANES analysis has shown that the vanadium ions in these superconducting oxides are in pentavalent state. As mentioned above, thallium shows two valencies, Tl\textsuperscript{1+} and Tl\textsuperscript{3+}. It would be therefore interesting to see whether the vanadium doping on Tl ion sites in the superconducting oxides forces Tl to change its atomic environment. It is with this aim, we have undertaken the study of Tl L\textsubscript{I}, L\textsubscript{II} and L\textsubscript{III} edges in some model compounds and in thallium based superconductors. In particular, we have measured the L\textsubscript{I}, L\textsubscript{II} and L\textsubscript{III} absorption spectra of thallium in model compounds namely TlCl, TlBr, TlI, Tl\textsubscript{2}CO\textsubscript{3}, TlNO\textsubscript{3}, Tl\textsubscript{2}SO\textsubscript{4}, Tl(CH\textsubscript{3}COO), Tl(C\textsubscript{6}H\textsubscript{5}COCHCOCH\textsubscript{3}), Tl(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2}), Tl\textsubscript{2}Ta\textsubscript{2}O\textsubscript{6}, Tl\textsubscript{2}O\textsubscript{3}, Tl(NO\textsubscript{3})\textsubscript{3}.3H\textsubscript{2}O, Tl(CH\textsubscript{3}COO)\textsubscript{3}, Tl(CF\textsubscript{3}COO)\textsubscript{3} and Ba\textsubscript{2}Tl\textsubscript{2}O\textsubscript{5} and superconducting oxides of composition Tl\textsubscript{1-x}V\textsubscript{x}Sr\textsubscript{2}(Ca\textsubscript{0.8}Y\textsubscript{0.2})Cu\textsubscript{2}O\textsubscript{y}, where x = 0.2, 0.3, 0.4 and 0.5. In addition to these oxides, we have also examined the L\textsubscript{I}, L\textsubscript{II}, and L\textsubscript{III} edge spectra in Tl\textsubscript{0.5}Pb\textsubscript{0.5}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7}, TlBa\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7}, Tl\textsubscript{2}Ba\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8}, and Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10}.

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6.2. RESULTS AND DISCUSSION

In Figures 6.1-6 are presented the normalized $L_{III}$ and $L_I$ absorption spectra of model thallium compounds and superconducting oxides containing thallium studied in this work. The procedure used for normalizing these XANES spectra is similar to that employed for the study of vanadium compounds.

As mentioned below, these normalized X-ray absorption spectra suggest at once that the XANES of $L_{III}$ edge of monovalent and $L_I$-edges of both monovalent and trivalent compounds have far fewer features as compared to $L_{III}$ - edge of trivalent thallium compounds. We shall first discuss the thallium $L_{III}$-edge spectra. It may be stated here that the $L_{II}$-edge spectra of thallium are very similar to $L_{III}$-edge spectra. Therefore, the profiles of $L_{II}$-edges are not given here. We could not record the $L_I$, $L_{II}$ and $L_{III}$ absorption spectra of pure thallium metal since it gets easily oxidized in air at normal temperatures\(^2\). The profiles of L absorption edges reported in the above figures are obtained by averaging the results of a very large number of spectra recorded in turn from each sample.

We see in Figure 6.2 that the $L_{III}$ absorption discontinuity of thallium in trivalent thallium compounds splits into three components whereas no splitting is observed in $L_{III}$ - edges in monovalent compounds (Figure 6.1). $L_I$ - edge spectra of both the monovalent and trivalent thallium compounds show no splitting (Figures IV.3-4). For plotting purpose the inflection point on the $L_{III}$ - edge in $\text{Tl}_2\text{O}_3$ is taken as a reference point. Its energy is found to be $12665.00 \pm 0.50 \text{ eV}$. Energy calibration was done by assigning the energy $12654.50 \text{ eV}^{15}$ to the inflection point on the K - edge of pure selenium metal recorded for this purpose. This calibration was also checked by assigning the energy $12063.40 \text{ eV}$ to the peak position of tungsten $L_{4\gamma}$ emission line.
Figure 6.1: Normalized Tl L\textsubscript{III} absorption spectra of Tl\textsubscript{2}Ta\textsubscript{2}O\textsubscript{6}, TlCl, TlBr, TlI, TlNO\textsubscript{3}, Tl\textsubscript{2}CO\textsubscript{3}, Tl\textsubscript{2}SO\textsubscript{4}, Tl(CH\textsubscript{3}COO), Tl(C\textsubscript{6}H\textsubscript{5}COCHCOCH\textsubscript{3}) and Tl(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})
Figure 6.2: Normalized Tl $L_{III}$ absorption spectra of Tl$_2$O$_3$, BaTl$_2$O$_5$, Tl(CH$_3$COO)$_3$, Tl(CF$_3$COO)$_3$ and Tl(NO$_3$)$_3$·3H$_2$O
Figure 6.3: Normalized Tl $L_I$ absorption spectra of $\text{Tl}_2\text{Ta}_2\text{O}_6$, $\text{TlCl}$, $\text{TlBr}$, $\text{TlI}$, $\text{TlNO}_3$, $\text{Tl}_2\text{CO}_3$, $\text{Tl}_2\text{SO}_4$, $\text{Tl}(\text{CH}_3\text{COO})$, $\text{Tl}(\text{C}_6\text{H}_5\text{COCHCOCH}_3)$ and $\text{Tl}(\text{C}_5\text{H}_7\text{O}_2)$
Figure 6.4: Normalized Tl $L_I$ absorption spectra of Tl$_2$O$_3$, BaTl$_2$O$_5$, Tl(CH$_3$COO)$_3$, Tl(CF$_3$COO)$_3$ and Tl(NO$_3$)$_3$.3H$_2$O.
Figure 6.5: Normalized Tl L_{III} absorption spectra of TlBa_{2}CaCu_{2}O_{7}, Tl_{0.5}Pb_{0.5}Sr_{2}CaCu_{2}O_{7}, Tl_{2}Ba_{2}CaCu_{2}O_{8}, TlBa_{2}Ca_{2}Cu_{3}O_{10} and Tl_{1-x}V_{x}Sr_{2}(Ca_{0.8}Y_{0.2})Cu_{2}O_{y}, (x = 0.2, 0.3, 0.4, 0.5)
Figure 6.6: Normalized Tl $L_I$ absorption spectra of TlBa$_2$CaCu$_2$O$_7$, Tl$_{0.5}$Pb$_{0.5}$Sr$_2$CaCu$_2$O$_7$, Tl$_2$Ba$_2$CaCu$_2$O$_8$, TlBa$_2$Ca$_2$Cu$_3$O$_{10}$ and Tl$_{1-x}$V$_x$Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_y$, ($x = 0.2, 0.3, 0.4, 0.5$)
It may be mentioned here that the thallium $L_{III}$ - edge spectra in Tl, TlCl, TlBr, Tl$_2$O$_3$, Tl(NO$_3$)$_3$, Tl$_2$(SO$_4$)$_3$ and Tl(CH$_3$COO) were recorded by Agarwal and Verma on a Cauchois - type bent crystal X-ray spectrograph using photographic technique. These workers have given the microphotometer traces of $L_{III}$ edges in TlCl, TlBr, and Tl(NO$_3$)$_3$ only. Since these spectra are recorded on a low-resolution spectrograph and their microphotometer traces show a lot of noise in the recorded spectra it is difficult to compare our spectra with them. Studer et al. have reported X-ray absorption spectra for some thallium compounds and the profiles are given for TlBr, Tl$_2$Ta$_2$O$_6$ and Tl$_2$O$_3$. Vijayakrishnan et al. studied $L_{III}$ -edge spectra in TlCl, TlNO$_3$ and Tl$_2$CO$_3$. The spectra for the compounds studied in the present investigation are similar to the spectra reported by Studer et al. and Vijayakrishnan et al.

6.2.1 THALLIUM $L_{III}$ - EDGE SPECTRA

Thallium $L_{III}$ - edge spectra for monovalent compounds are reported in Figure 6.1. In Figure 6.2 are given the $L_{III}$ edge spectra for trivalent thallium compounds. Figure 6.1 shows a single absorption peak while the spectra in Figure 6.2 shows a weak peak followed by a shoulder on rising absorption which culminates into a strong absorption peak.

The outer electronic configuration of monovalent thallium is $6s^26p^06d^0$ and hence the single absorption peak observed in the monovalent thallium compounds viz. TlCl, TlBr, TlI, Tl$_2$CO$_3$, Tl(NO$_3$)$_3$, Tl$_2$Ta$_2$O$_6$ corresponds to the allowed transition of $2p_{3/2}$ electron to 6p state which is admixed with 6d and 2s characters of metal and ligands respectively. On the other hand following the electronic assignment schemes invoked by Retoux et al. and Heald et al. for $L_{III}$ absorption edge features 6s, 6p and 6d states being completely vacant in trivalent thallium compounds, the weak peak, the shoulder and the main absorption peak can be
attributed to the transitions $2p_{3/2} \rightarrow 6s$, $2p_{3/2} \rightarrow 6d (t_{2g})$ and $2p_{3/2} \rightarrow 6d (e_g)$ respectively. The final states of the latter transition are admixed with $6p$ from metal and $2s$ and $2p$ characters from ligand. It is interesting to note that the shoulder peak of trivalent compounds and the main absorption peak of monovalent compounds occur almost at same energy. The important difference between the spectra of monovalent and trivalent compounds is the 4 eV shift in the inflection point energy of $L_{III}$ edges and a 12 eV energy shift of main absorption maxima is clearly seen in the figures. It is surprising that in monovalent thallium compounds, 6d being vacant, a peak corresponding to the electronic transition, $2p_{3/2} \rightarrow 6d$ is not observed. In fact, the transition probability for $p \rightarrow d$ transition is more as compared to that for $p \rightarrow s$ transition. It may be mentioned here that Studer et al. and Rao and Wong have studied L-edge spectra in thallium and lead compounds respectively and assigned such electronic transitions to the spectral features observed.

On the basis of these absorption spectra of thallium model compounds, one can distinguish between the monovalent and trivalent thallium ions in the superconducting oxides. We shall first determine the valence state of thallium ions in a well-characterized superconductors.

The $L_{III}$-absorption spectra of Tl$_{0.5}$Pb$_{0.5}$Sr$_2$CaCu$_2$O$_7$, TlBa$_2$CaCu$_2$O$_7$, Tl$_2$Ba$_2$CaCu$_2$O$_8$ and Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ superconductors are shown in Figure 6.5. The overall profiles of these oxides are very similar to those of Tl$_2$O$_3$ and other trivalent thallium compounds suggesting octahedral environment of ligands around trivalent thallium ions. However, from a more careful examination of intensities and energies of the peaks in the $L_{III}$-edge region, it is found that they are slightly different from those observed for trivalent compounds. This seems to suggest that the octahedron of ligands around the thallium ions is distorted. This
sort of distortion can be studied in detail if we analyze the EXAFS spectrum associated with the $L_{III}$-edge. This is done in the next section of this Chapter. These observations on the whole, clearly indicate the presence of octahedrally coordinated $\text{Tl}^{3+}$ ions in these four well-characterized superconducting oxides. Our results in this respect are in good agreement with those obtained by Studer et al$^{17,18}$ It may be interesting to mention here that on the basis of the crystal structures of these oxides Studer et al have ruled out the possibility of existence of $\text{Tl}^{1+}$ ions. However, it is possible that the holes may be delocalized on an oxygen p-like valence band. According to the theoretical considerations of the Cu-O sheets, holes are more or less delocalized in the in-plane non-bonding oxygen p band formed by orbitals pointing towards the centre of the negative oxygen square, so that Tl(I) configuration appears to be one of the possibilities for doping. However, from the similarity of the X-ray spectra of superconducting oxides and $\text{Tl}_2\text{O}_3$, there is absolutely no doubt that $\text{Tl}^{3+}$ ions exist in such oxides, as has been shown by us as well as by Studer et al$^{17,18}$. 

After having confirmed the presence of $\text{Tl}^{3+}$ ions in well characterized superconducting oxides, we will now determine the valence state of Tl ions in $\text{Tl}_{1-x}\text{V}_x\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$. The X-ray absorption spectra in Figure 6.5 show similarity with the spectra of $\text{Tl}_2\text{O}_3$, suggesting thereby the presence of $\text{Tl}^{3+}$ ions in octahedral configuration in these oxides. The slight reduction of intensity and increase of energy of principal absorption maxima are also observed in these oxides. It is very difficult to give any reason for this, but it seems that the crystal structure has some relation to their absorption spectra. 

Vijaykrishnan et al$^{19}$ have noted that the shoulder-like feature of $\text{Tl}^{3+}$ compounds and the main peak in $\text{Tl}^{1+}$ compounds are in same energy region. This observation has also been noted by us.
In order to understand the features in the spectra of Ti cuprate superconductors in the region between the pre-edge peak and the main absorption peak, Vijaykrishnan et al. have recorded the Ti L\textsubscript{III} spectra of physical mixtures of Tl\textsubscript{2}CO\textsubscript{3} and Tl\textsubscript{2}O\textsubscript{3} in varying proportion. These authors observe that there is a progressive development of intensity in the region between the pre-edge peak and main absorption maximum. Furthermore, this feature shifts towards the main peak of Tl\textsuperscript{1+} with the increase in the proportion of Tl\textsubscript{2}CO\textsubscript{3}. The position of the main absorption peak due to Tl\textsubscript{2}O\textsubscript{3}, however seems to remain constant. On the basis of these observations, these authors have suggested that the above feature between the pre-edge and the main peak could be due to a Tl\textsuperscript{1-} like state different from a distinct localized Tl\textsuperscript{1+} species present in these cuprates. Their proposal of existence of Tl\textsuperscript{1+} like state in cuprate superconductors has some support from the X-ray photoemission studies of Suzuki et al. who have measured the Ti 4f core level binding energies in Tl\textsubscript{2}O, Tl\textsubscript{2}O\textsubscript{3} and Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10} in order to elucidate the chemical state of Ti ions in the superconducting oxides. The binding energies of Ti 4f level are found to be 118.6, 117.4 and 118.2 eV for Tl\textsubscript{2}O, Tl\textsubscript{2}O\textsubscript{3} and Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10} respectively, i.e., the binding energy of Ti 4f\textsubscript{7/2} level in Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10} is higher than that in Tl\textsubscript{2}O\textsubscript{3} but slightly lower than that in Tl\textsubscript{2}O. These authors concluded on the basis of binding energy data that the valence of Ti in the superconducting oxide Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10} is between 3\textsuperscript{+} and 1\textsuperscript{+}. It is not convincing that the binding energy of Tl\textsuperscript{+} ion is greater than the binding energy of Tl\textsuperscript{3+} ion. Moreover, no reason has been given by Suzuki et al. for this observation. In most of the compounds it is generally observed that the higher valent metallic ions show binding energies greater than those in lower valent metallic ions. We feel that authors could have measured the binding energies in a few more monovalent and trivalent thallium compounds before arriving at the final conclusion.
Li et al. have also carried out X-ray absorption measurements on Tl₂CO₃, Tl₂O₃, Tl₁₋ₓBiₓSr₂CuO₅ (x = 0.2, 0.5) and Tl₀.5Bi₀.5Sr₂CaCu₂O₇. The Tl LIII absorption edges of Tl₀.8Bi₀.2Sr₂CuO₅, Tl₀.5Bi₀.5Sr₂CuO₅ and Tl₀.5Bi₀.5Sr₂CaCu₂O₇ are at the lower energy side relative to the LIII edge in Tl₂O₃. Although the edge shifts in these compounds are most likely due to changes in the effective charge of Tl ions, the possibility of other origins (e.g., coordination geometry related) cannot be ruled out. Interestingly, the pre-edge feature is significantly lower in Tl₂O₃ than in the other non-Tl¹⁺ compounds. These authors attribute this to a combination of two effects: the edge feature in the superconducting compounds is riding higher on the edge-step which has been down-shifted by the decrease in Tl valence; and a decrease in the width of the 6s-orbitals the pre-edge feature has occurred in these compounds. If the Tl valence in the Tl-based cuprates is less than 3⁺, it would be possible for the Tl 6s level to cross the Fermi level, even though the band structure calculations show that the Tl 6s level in the single Tl-0 layered compounds including Tl₁₋ₓBiₓSr₂CuO₅ and Tl₀.5Bi₀.5Sr₂CaCu₂O₇ is above the Fermi level. However, careful examination of the L₁-edge profiles, (presented in the next section) the possibility of presence of monovalent thallium ions in these cuprate superconductors can be ruled out clearly.

Studer et al. reported the Tl LIII-edge spectra of thallium in cuprate superconductors containing thallium. They interpret the experimentally observed spectral features of LIII-edge in terms of the Tl-0 distances in these systems using Natoli's multiple scattering approximation. They find Tl-0 distances similar to those in Tl¹⁺-0 distances in cuprates but conclude that the Tl¹⁺ state is absent within the experimental error (± 10%). It may be noted that one finds both Tl¹⁺-0 and Tl³⁺-0 type distances in the cuprates since Tl has a highly distorted oxygen octahedra. It is the view of Vijayakrishnan et
that the presence of different distances can by no means be used as an argument in favour of or against the presence of Tl\textsuperscript{1+} or any such species. They argued that in Bi cuprates also one finds distances close to those of Bi\textsuperscript{3+}-O and Bi\textsuperscript{5+}-O although there is no Bi\textsuperscript{5+} in these cuprates. Furthermore, these authors have commented that Studer et al\textsuperscript{17} have not discussed the pre-edge feature in the spectrum of Tl\textsubscript{2}O\textsubscript{3} or its closeness to the main peak of Tl\textsuperscript{1+} compounds. However, we do find in one of the papers of Studer et al\textsuperscript{17,18}, a detailed discussion on the feature B.

Our results support the proposal of existence of Tl\textsuperscript{3+} state in the thallium doped cuprate superconductors. This can be clearly seen by the L\textsubscript{I} edge profiles, presented in the next Section. It may be noted that Vijayakrishnan et al\textsuperscript{19} have not studied the L\textsubscript{I} edge profiles in these superconductors. Moreover, we feel that the L\textsubscript{III} edge profiles of physical mixture of compounds Tl\textsubscript{2}CO\textsubscript{3} and Tl\textsubscript{2}O\textsubscript{3} in different proportion may not give correct picture. Thus, for example the L\textsubscript{III} edge spectrum of the mixture, 60\% Tl\textsubscript{2}CO\textsubscript{3} (containing 60\% Tl\textsuperscript{1+}) and 40\% Tl\textsubscript{2}O\textsubscript{3} (40\% Tl\textsuperscript{3+}) will be very much different from the spectrum generated from the 60\% \( \mu \) vs. \( E \) curve of Tl\textsubscript{2}CO\textsubscript{3} and 40\% \( \mu \) vs. \( E \) curve of Tl\textsubscript{2}O\textsubscript{3}, as has been shown by Anjli et al\textsuperscript{35} in cuprate superconductors. A better way of doing this is to synthesize a compound wherein Tl exists in both valence states and record its L\textsubscript{III} edge spectrum. However, it is very difficult to prepare such compound in our laboratory. We therefore have not done this sort of analysis.

### 6.2.2 Thallium L\textsubscript{I} Edge Spectra

The L\textsubscript{I} edge spectra for the monovalent and trivalent compounds and superconducting oxides are given in Figs 6.3, 4, and 6. Here, the edge profile is simple in all the cases. Splitting of the edge is not at all observed. The only difference
in monovalent and trivalent thallium compounds is that the inflection point shift is about $4 \pm 0.5$ eV and main absorption peak shift is about $12 \pm 0.5$ eV. In monovalent compounds, 6s orbital is occupied, but 6p is completely vacant. The main absorption peak observed in these monovalent compounds (Figure 6.3) corresponds to 2s → 6p transition and since 6s is being unavailable for transition to occur, no splitting of the $L_I$ edge is visible. In trivalent compounds, the 6s and 6p orbitals being vacant, a pre-edge peak corresponding to the forbidden transition, 2s → 6s is expected to be observed. However, we have not observed such peaks. Here in this case, like the monovalent compounds, only the main absorption peak is observed. This peak corresponds to 2s → 6p (the pre-peak being absent).

The $L_I$ edge spectra of all the superconducting oxides, $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7$, $\text{TlBa}_2\text{CaCu}_2\text{O}_7$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, $\text{Tl}_2\text{Ba}_2\text{CaCu}_3\text{O}_{10}$ and $\text{Tl}_{1-x}\text{V}_x\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ where $x = 0.2, 0.3, 0.4$ and $0.5$ are similar to those in $\text{Tl}_2\text{O}_3$ and other trivalent compounds. It is also observed that the main absorption peaks are located at the same energy. The only noticeable difference is the intensity of peak corresponding to 2s → 6p transition. The intensity of this peak is slightly less in superconducting oxides as compared to that in $\text{Tl}_2\text{O}_3$. Similar results have been obtained by Studer et al.\textsuperscript{17,18} in 1212, 2212, 1223 and 2223 superconducting oxides. Thus, the results of $L_I$ XANES also lead us to conclude that the octahedrally coordinated thallium ions exist in $3^+$ state in superconducting oxides. In other words, it means that they are in the 6s levels.

6.2.3 SHAPE RESONANCE REGION OF ABSORPTION

A well characterized absorption peak beyond the first absorption minimum of the K-edge spectra of elements is often ascribed to shape resonances\textsuperscript{36-38}. These absorption peaks arise as a consequence of the potential barrier created by the ligand
electrons. The presence of a potential cage forces the atomic states to exist either entirely inside or outside the cages. The inside states, better known as inner well states, are energetically capable of evolving into continuum states. However, they are compressed into the shape of the ligand cage so that they can produce sufficient overlap with the initial 1s states and hence give rise to shape resonance absorption. Extending the same arguments to L_\text{I} edge spectra, we may consider the absorption features in the region of 25-40 eV in the monovalent thallium salts as due to shape resonances arising from 2s electron excitation to quasi bound states having a p character. Our studies in this region do not suggest useful generalizations of any kind since this energy range also falls within the XANES \rightarrow EXAFS transition region. This could also be due to a variety polyhedral environments around the Tl^{1+} ions in the compounds investigated. However we note that in the highly ionic thallium nitrate, in which the coordination polyhedron is both large and highly symmetrical, the shape resonance peak is relatively well defined (see Figure 6.3). The shape resonances are ill defined when covalency dominates the nature of bonding as in TlII, and when the symmetry of the coordination polyhedron is low.

L_{\text{III}} edge spectra also exhibit an absorption feature attributable to shape resonance in the same energy region. Such transitions are possible if the quasi bound states have sufficient d character in them. It is plausible because in the Xa-MSW calculations which have been used with success to simulate such spectra, the wave functions employed do include such higher angular momentum states in them.

6.3. THALLIUM L_{\text{III}} - EDGE EXAFS SPECTRA

Since no single crystal structure data are available on the superconducting oxides, Tl_{1-x}V_xSr_2(Ca_{0.8}Y_{0.2})Cu_2O_y studied in this investigation, we thought it worthwhile to measure the EXAFS
at thallium L\textsubscript{III} edges and analyze the data using Fourier transform and non-linear curve fitting techniques in order to get structural information on these complex oxides.

We have used Tl\textsubscript{2}O\textsubscript{3} as a model compound containing Tl-0 atom pair. The Fourier transforms of L\textsubscript{III} edge EXAFS spectra for Tl\textsubscript{2}O\textsubscript{3}, Tl\textsubscript{2}Ta\textsubscript{2}O\textsubscript{6} and Ba\textsubscript{2}Tl\textsubscript{2}O\textsubscript{5} are shown in Figure 6.7 and in Figure 6.8 are given the Fourier transforms of EXAFS spectra for TlBa\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7}, Tl\textsubscript{0.5}Pb\textsubscript{0.5}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{7}, Tl\textsubscript{2}Ba\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8}, Tl\textsubscript{2}Ba\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{10} and Tl\textsubscript{1-x}V\textsubscript{x}Sr\textsubscript{2}(Ca\textsubscript{0.8}Y\textsubscript{0.2})Cu\textsubscript{2}O\textsubscript{y} where x = 0.2 and 0.5.

The Fourier transform of the L\textsubscript{III}-edge EXAFS data in Tl\textsubscript{2}O\textsubscript{3}, presented in Figure 6.7 shows three distinct peaks. The first peak is the dominant one and corresponds to Tl-0 distance. Its intensity is large as compared to the others. (The small peaks on large R side (R > 4.5 Å) in the Fourier transform are most likely resulted from an improper background removal at large k values.) This dominant peak in Tl\textsubscript{2}O\textsubscript{3} was inverse Fourier transformed to yield the contribution of backscatterers about Tl\textsuperscript{3+} ions.

To determine the local structure of Tl\textsuperscript{3+} ions in the superconducting oxides, as mentioned earlier, we use Tl\textsubscript{2}O\textsubscript{3} as the reference compound to model the Tl\textsuperscript{3+} structure in oxide environment. In the single-scattering approximation\textsuperscript{39-41}, the observed EXAFS $\chi(k)$ may be described by

$$\chi(k) = \frac{-1}{k} \sum_j A_j \sin \left[ 2R_j k + \phi_j(k) \right]$$

having oscillatory terms with frequencies $[2R_j k + \phi_j(k)]$, and amplitude terms $A_j$ is given by

$$A_j = \left( N_j / R_j^2 \right) f_j(\pi,k) \exp(-\sigma_j^2 k^2).$$

The parameters on the right hand side of equations 6.1 and 6.2 may be classified as (a) scattering parameters which include

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Figure 6.7: Fourier transforms of the thallium L_{III}-edge EXAFS in Tl₂O₃, Tl₂Ta₂O₆ and BaTl₂O₅.
Figure 6.8: Fourier transforms of the thallium \( \text{L}_{\text{III}} \)-edge EXAFS in \( \text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7 \), \( \text{TlBa}_2\text{CaCu}_2\text{O}_7 \), \( \text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8 \), \( \text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) and \( \text{Tl}_{1-x}\text{V}_x\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y \), \( x = 0.2 \) and 0.5
phase shift $\phi_j(k)$, backscattering amplitude $f_j(\pi,k)$ and mean free path $\lambda$ and (b) structural parameters which include coordination number $N_j$, Debye-Waller type factor $\sigma_j$ and bond distance $R_j$. The summation is over all coordination shells $j$ participating in the EXAFS event. In a model system such as $\text{Tl}_2\text{O}_3$ for which crystallographic data are available, i.e. coordination number $N_j$, the interatomic distance $R_j$ and Debye-Waller factor $\sigma_j$ are known, its EXAFS spectrum may be used to generate a set of self-consistent scattering parameters, which can then be transformed to an unknown system of similar chemical nature to determine structural parameters for the unknown.

A least-squares procedure is set up to minimize the variance $S$, where

$$S = \sum_{i=1}^{N} (\chi_i^F - \chi_i)^2$$

(6.3)

Here $\chi_i^F$ are the Fourier-filtered experimental data and $\chi_i$ is the analytical expression given in equation (6.1) which describes $\chi_i^F$ for $N$ data points. Since $\chi(k)$ is not a linear function of the various parameters, a Taylor series expansion is used which expresses $\chi(k)$ in terms of approximate parameter values, $P_j$ and parameter adjustments, $\Delta P_j = P_j - P_j'$. When the least-squares condition is applied, a set of simultaneous equations is obtained in terms of $\Delta P_j$ rather than $P_j$. The equations are solved for the adjustment $\Delta P_j$, and the parameters were adjusted by $\Delta P_j$ to give a new set of estimates. The procedure was then reiterated with a new estimate $P_j$ and so on until the new solution differed from the last by less than a desired value, which is usually 1%.

### 6.3.1 Determination of Tl-O Phase Shift and Envelope Function for Oxygen

Crystalline $\text{Tl}_2\text{O}_3$ is isostructural with $\text{CaF}_2$. It is related to that of $\text{CaF}_2$, from which it may be derived by removing one-quarter of the anions and the rearranging the atoms somewhat.
The six coordinated Tl atoms are of two types. Instead of 8 neighbours at the vertices of a cube, two are missing. For one quarter of the Tl atoms these two are at the ends of a body-diagonal, and for the remainder at the ends of a face-diagonal. Both coordination groups may be described as distorted octahedron. In the first coordination group, thallium is linked to six oxygen ions at a distance of 2.26 Å and in the second, it is coordinated to four oxygen atoms in the range 2.13 Å - 2.18 Å and two at 2.47 Å.

To elucidate the structural environment of thallium giving rise to the observed EXAFS in the superconducting oxides, we first use the above structural parameters for Tl₂O₃ in the curve fitting analysis of Fourier-filtered EXAFS in the region 0.8 - 2.3 Å.

From the Tl L₃-edge EXAFS data, it is clear that the first radial peak in the region 0.8 - 2.3 Å of the Fourier transform for Tl₂O₃ shown in Fig 6.7, corresponds to the shell of six O atoms about the absorbing Tl atom in the C-M₂O₃ -type crystal structure. The inverse transform in Figure 6.9 indeed shows an experimental envelope characteristic of a low Z backscattering atom, i.e. oxygen. To obtain self consistent phase shifts for the Tl-O atom pair, the values of Teo and Lee ²²,⁴³-⁴⁴ in the form

\[ \phi_j(k) = P_0 + P_1 k + P_2 k^2 + P_3 / k^3 \]  (6.4)

were used as the initial inputs. The envelope function \( f_j(\pi,k) \exp(-2R_j/\lambda) \) for oxygen was obtained empirically from the filtered EXAFS itself [Figure 6.9] and was fixed in the simulation. \( E_0 \), the inner potential or the threshold energy required to determine the value of photoelectron wave-vector, \( k \), was found to be - 12659 eV. It is obtained⁴⁴ after matching the peaks in imaginary part and modulus of the Fourier transform. \( N = 6 \) and \( R = 2.25 \) Å were used as fixed structural parameters. The
Figure 6.9: Inverse Fourier transform (*** *) and simulated EXAFS of the first FT peak (solid line) for Tl$_2$O$_3$. 
thermal parameter $\sigma_j$ was varied. The simulation was done in $k$ space to emphasize the backscattering contribution of oxygen at low $k$. The results are shown in Fig 6.9, where the curve (solid line) denotes the Fourier filtered spectrum and the points denote the simulated spectrum. The input values of $N$ and $R$, the phase parameters and the thermal parameter determined in the fitting are

$$P_0 = 5.148 \quad P_1 = -1.083 \quad P_2 = 0.025 \quad P_4 = 52.03$$

$$\sigma_j = 0.002 \quad N_j = 6 \quad R_j = 2.25 \text{ Å}^0$$

The computer simulation was fitted with a standard deviation of 5% of the maximum amplitude of the experimental $\chi^F(k^3)$. The plot of experimental phase shift versus wave vector $k$ for Tl-O atom pair obtained in the simulation is shown in Figure 6.10(a). We have plotted in Figure 6.10(b), the phase shift data of Teo and Lee. Central atom phase shift for $l = 2$ are not given by these authors for thallium. Therefore the phase shifts for Tl were obtained by interpolation as suggested by these authors themselves. It is to be noted that in the theoretical plot, $4\pi$ has been added to the values of phase shifts for the comparison. It is seen from the Figure 6.10(a) and Fig 6.10(b) that the experimentally determined phase shift curve for Tl-O atom pair is very close to that obtained from theoretical values given by Teo and Lee.

6.3.2 THALLIUM ENVIRONMENT IN Tl$_2$Ta$_2$O$_6$ AND Ba$_2$Tl$_2$O$_5$

The phase shifts for Tl-O pair and envelope function for oxygen extracted from the filtered experimental $L_{III}$-edge EXAFS of crystalline Tl$_2$O$_3$ as described above were then transferred and used to determine $N$, $R$ and $\sigma$ in two well known crystalline compounds namely Tl$_2$Ta$_2$O$_6$ and Ba$_2$Tl$_2$O$_5$. Curve fitting was
Figure 6.10: (a) Phase shifts for Tl-O atom pair: Experimental
Figure 6.10: (b) Phase shifts for Tl-O atom pair: Theoretical
Figure 6.11: Inverse Fourier transform (*) and simulated EXAFS of the first FT peak (solid line) for Ti$_2$Ta$_2$O$_6$.
Figure 6.12: Inverse Fourier transform (**) and simulated EXAFS of the first FT peak (solid line) for Ba$_2$Ti$_2$O$_6$
there are only four oxygen atoms. This number agrees reasonably well with that determined from X-ray diffraction measurements. The two distant oxygen atoms at 2.41 A° reported from diffraction measurements appear to form a second coordination shell surrounding the thallium ion.

6.3.3 THALLIUM ENVIRONMENT IN SUPERCONDUCTING OXIDES

We shall first briefly discuss the structural studies carried out on the superconducting oxides studied in this work.

The recent discovery by Sheng and Hermann of superconductivity in the Tl-Ca-Ba-Cu-O system has sparked numerous investigations of the phases present in this system. It is now known that superconducting phases in this system can be represented as $Tl_mBa_{2n-1}Ca_nCu_{n+2}O_{m+2(n+1)}$, where $m = 1, 2$ and $n$ is the number of consecutive Cu-O layers. Values of $n$ range from 1 to 3 in bulk phases but can range up to at least 5 on a microscopic level. The superconducting transition temperature, $T_c$, is about 125K for the $n = 3$ and $m = 2$ phase and appears to be about 140K for the $n = 5$ phase.

From X-ray single crystal data, the structures of the phases, with $n = 1, 2$ and 3 have been solved and refined. The unit cells are tetragonal, space group I4/mmm, with $a \approx 3.85$ A° and $c \approx 23.2, 29.3$ and 35.9 A° respectively. No evidence was found for any superlattice peaks indicative of an enlarged cell ($a = 5.44$ A°) in either the single crystal data or in X-ray powder diffraction measurements on bulk samples.

The structures are comprised of single, double or triple CuO$_2$ sheets, with Cu in the square planar coordination, that alternatively stack with sheets of barium ions and double sheets of Tl-O atoms. When Ca is present, it is found between the Cu-O sheets. There is considerable disorder of the oxygen atoms in the Tl-O sheets in the form of displacements of about 0.4 A° from the ideal positions. (The compound with $m=2$ and $n=3$ viz. 180
Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ (2223) possesses the highest known Tc of 125K. In short, these phases possess a layered structure with distorted rock salt-type layers of T1O and oxygen-deficient perovskite-type layer (ACuO$_{3-y}$) with A= Ba, Ca.

TlBa$_2$CaCu$_2$O$_7$ (also called "1212-phase") is a member of the structural series (T1O)$_m$Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2+2n}$, where m = 1 and n = 2, i.e., it contains T1O single-layers and two consecutive CuO$_2$ layers that are separated by a Ca layer. The layer sequence Ca-CuO$_2$-BaO-CuO$_2$-Ca etc leads to a translation period perpendicular to the layers of 12.75 Å and to a prominent low-angle reflection at 2θ = 6.94 Å (Cu Kα) in the X-ray diffraction pattern$^{56}$. The structure contains one thallium site with flattened octahedral oxygen coordination, one calcium site with deformed cubic, one barium site with nine-fold (capped square-antiprismatic), and one copper site with square-pyramidal oxygen coordinations and three oxygen sites. The two short Tl-O and four long Tl-O distances in this phase are 2.01 and 2.73 Å respectively and considerable disorder in the Tl and Ba sites has been reported. Ganguli et al$^{57}$ found no such disorder in Tl$_{0.5}$Pb$_{0.5}$CaSr$_2$Cu$_2$O$_7$, and the Tl/Pb-O distances to be much shorter, being 1.98 and 2.71 Å. Moreover, these authors commented that the introduction of Pb in the Tl layers makes the bonds considerably more covalent and that the shorter Cu-O distances obtained from neutron diffraction measurements seem to be related to the higher Tc of this cuprate superconductor.

Refined structural data on Tl$_2$Ba$_2$CaCu$_2$O$_8$ are reported from single-crystal X-ray diffraction by Subramanian et al$^{49}$ and Onodo et al$^{58}$ and from neutron powder diffraction by Cox et al$^{51}$. The structure has body centerd tetragonal symmetry and shows relatively large variations in the c parameter. It contains one thallium site with deformed octahedral oxygen coordination, one barium site with nine-fold, one calcium site with nearly cubic, and one copper site with square-pyramidal oxygen coordination,
and three oxygen sites of which that constituting the $Tl_2O_2$
layers is shifted away from its average site $4e$ by about $0.5$
Å. The thallium ions are coordinated to one oxygen atom at $1.983$
Å, one at $2.022$ Å, two at $2.470$ Å and two at $3.027$ Å.

The superconducting oxide, $Tl_2Ba_2Ca_2Cu_3O_{10}$ (also called
"2223 - phase") contains $Tl_2O_2$ double layers and three
consecutive $CuO_2$ layers that are separated by two calcium layers.
The structure of this compound has tetragonal symmetry $^{54}$ and
contains one thallium site with distorted octahedral oxygen
coordination, one barium site with nine fold, one calcium site
with nearly cubic and two copper sites with square planar ($Cu1$)
and square-pyramidal ($Cu2$) oxygen coordinations respectively and
four oxygen sites. The $Tl$ site has defects or is partially
occupied by $10\%$ calcium $^{51}$. The bond distances within $Tl0$
single-layers at $150$ K are $Tl-O = 2.47$ and $3.01$ Å, those between
the two $Tl0$ single-layers are $2.017$ Å and those between the
$Tl_2O_2$ and $CuO_2$ layers are $1.944$ Å.

The Fourier transforms for $TlBa_2CaCu_2O_7$, $Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$, $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$ are shown in Figure 6.8. The first and the strongest peak in the transform
of the first two compounds is the signal from the first
coordination shell of oxygen atoms around each thallium atom. The
two transforms are almost similar to each other because of
similarity of their crystal structure. To interpret these data we
have used the Fourier filtered data from $Tl_2O_3$ standard to obtain
the backscattering amplitude of oxygen and $Tl-O$ atom pair phase
shift as a function of wave vector $k$. A non-linear least-squares
fitting technique was then employed to match the calculated $\chi(k)$
to the measured one obtained from inverse Fourier transform of
the first peak in Fig 6.8. The results of this first-shell
fitting for the two compounds are shown in Fig 6.13 (a and b)
Figure 6.13: (a) Inverse Fourier transform (*) and simulated EXAFS of the first FT peak (solid line) for TlBa$_2$CaCu$_2$O$_{7}$
Figure 6.13: (b) Inverse Fourier transform (*) and simulated EXAFS of the first FT peak (solid line) for Tl$_{0.5}$Pb$_{0.5}$Sr$_2$CaCu$_2$O$_7$
and the structural parameters determined from the fitting are

<table>
<thead>
<tr>
<th></th>
<th>(N_j)</th>
<th>(R_j(\text{A}^\circ))</th>
<th>(\sigma_j(\text{A}^\circ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{TlBa}_2\text{CaCu}_2\text{O}_7)</td>
<td>2.15</td>
<td>2.04</td>
<td>0.003</td>
</tr>
<tr>
<td>(\text{Tl}<em>{0.5}\text{Pb}</em>{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7)</td>
<td>2.10</td>
<td>1.99</td>
<td>0.006</td>
</tr>
</tbody>
</table>

The validity of the fitting procedure is proven by the excellent agreement between the structural parameters obtained by the analysis of EXAFS spectra and the X-ray diffraction values for these compounds\(^{56-57}\). We have also isolated the second peak in both these compounds and by transforming the peak to \(k\)-space and by performing the non-linear least-squares analysis, we find the \(\text{Tl}-0\) bond distances of 2.72 and 2.71 \(\text{A}^\circ\) respectively for the above oxides. However, there is a large uncertainty in the determination of near-neighbours. These numbers are 4.7 and 4.5. This may be due to the overlapping of second oxygen shell (2.75 \(\text{A}^\circ\)) with other shells on higher \(R\) side as well as due to the higher Debye-Waller factor.

As can be seen from the Fourier transforms in Figure 6.8 there are four peaks in the case of \(\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8\) and three peaks in \(\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}\). The first-shell fitting results presented in Figure 6.14 (a and b) and the parameters obtained in the fitting are

<table>
<thead>
<tr>
<th></th>
<th>(N_j)</th>
<th>(R_j(\text{A}^\circ))</th>
<th>(\sigma_j(\text{A}^\circ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8)</td>
<td>1.97</td>
<td>2.02</td>
<td>0.001</td>
</tr>
<tr>
<td>(\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}<em>3\text{O}</em>{10})</td>
<td>1.05</td>
<td>2.10</td>
<td>0.004</td>
</tr>
</tbody>
</table>
Figure 6.14: (a) Inverse Fourier transform (*** *) and simulated EXAFS of the first FT peak (solid line) for Tl$_2$Ba$_2$CaCu$_2$O$_8$
Figure 6.14: (b) Inverse Fourier transform (• • •) and simulated EXAFS of the first FT peak (solid line) for Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$

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For $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$, the intensity of the first peak is large as compared to that in $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{O}_{10}$. It can been seen from the values of bond distance and coordination number that there is a good agreement between our results for $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ and those obtained from X-ray and neutron diffraction measurements$^{49,51-54}$. However, for $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, though the Tl-O distance agrees with that reported, the number of near-neighbours is found to be one. One could expect two oxygen atoms to be coordinated to thallium ion. In all the four superconducting oxides, our results show that one or two oxygen atoms appear to be closer to the central thallium ion than those found from X-ray diffraction measurements. This could perhaps be due to the lack of precision on the oxygen atomic positions deduced from X-ray or neutron powder diffraction measurements. It may be mentioned here that in the case of 2212 superconducting oxide study by neutron diffraction, Subramanian et al$^{49}$ observed two very short Tl-O distances along the c-axis of the structure, i.e., the direction of the intergrowth, again in agreement with our EXAFS distance.

From the Fourier transforms of these compounds, it is difficult to estimate the number of second-nearest neighbours of thallium because of interference between the second oxygen shell (Tl-O distances at 2.47 and 3.027 Å) and the thallium shell (Tl-Tl distance at 3.70 Å) and the barium and copper shells between 3.5 and 3.8 Å. These second peaks (double-peak character) at larger distance in the above mentioned thallium bilayered compounds seem to be the characteristic of FT spectra of such compounds. It is to be noted that such double peak character in Fourier transformed spectra of monolayered compounds is absent.

The Fourier transform of $k^3\chi(k)$ of the Tl L$_{III}$ edge EXAFS of the two superconducting oxides of composition, $\text{Tl}_{1-x}\text{V}_x\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$ where $x = 0.2$ and 0.5, are shown in Figure 6.8. One major peak is seen in the Fourier transforms of
both the samples followed by two peaks of less amplitude. The position of this major peak is almost the same irrespective of the vanadium doping level. It can be attributed to the oxygen atoms surrounding thallium ion. The other peaks observed on the high R side may be due to the distant neighbours of thallium.

To get quantitative information, a curve fitting analysis was performed on the inverse Fourier transform of this peak in both the compounds (Figure 6.15 (a and b)). The simulated spectra are shown in Figure 6.15 and the Tl-O distances and coordination numbers obtained from this analysis are given below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( N_j )</th>
<th>( R_j (\text{A}^o) )</th>
<th>( \sigma_j (\text{A}^o) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0.2 )</td>
<td>2.20</td>
<td>2.01</td>
<td>0.002</td>
</tr>
<tr>
<td>( x = 0.5 )</td>
<td>2.10</td>
<td>2.03</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

The predicted number of oxygen atoms in the first coordination shells around thallium ion in both the compounds agree well with that expected for TlSr\(_2\)CaCu\(_2\)O\(_7\) or TlBa\(_2\)CaCu\(_2\)O\(_7\) structure. The Tl-O distances 2.01 and 2.03 A\(^o\), appear to agree with those in other superconducting oxides studied in this investigation. The distant peaks observed at 2.72 and 3.20 A\(^o\) also correspond to Tl-O interactions. Our results thus lead to the conclusion that the substitution of vanadium at Tl site does not change the local environment around thallium ion. Like TlBa\(_2\)CaCu\(_2\)O\(_7\), there exists a distorted octahedron of oxygen atoms around thallium ion. It may be interesting to mention here that the single crystal data are not hitherto available on these superconducting phases. Our results will be useful to the researchers working in the field of X-ray crystallography of these phases to arrive at the accurate values of coordination numbers, bond distances and structural disorders.
Figure 6.15: (a) Inverse Fourier transform (•••) and simulated EXAFS of the first FT peak (solid line) for Tl\(_{1-x}V_x\)Sr\(_2\)(Ca\(_{0.8}\)Y\(_{0.2}\))Cu\(_2\)O\(_y\), x = 0.2
Figure 6.15: (b) Inverse Fourier transform (*) and simulated EXAFS of the first FT peak (solid line) for $\text{Ti}_{1-x}\text{V}_x\text{Sr}_2(\text{Ca}_{0.8}\text{Y}_{0.2})\text{Cu}_2\text{O}_y$, $x = 0.5$
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