XAFS Studies and Chemical Shifts of Thallium L_{III} X-Ray Absorption Edges in Some of its Model Compounds and Superconducting Oxides

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Abstract. The position, shape and XAFS of X-ray absorption discontinuities have been used to deduce structural and chemical bonding information on model compounds of thallium and its superconducting oxides. It is observed that the L_{III} absorption edges of thallium shift towards the high energy side with respect to the position of the discontinuity in thallic oxide in all the systems investigated. The valence state of the metal ion in these compounds and electronegativity were compared in relation to chemical shifts. On the basis of our X-ray chemical shift data we have determined the valence state of the thallium ion in its superconducting oxides.

Keywords: Thallium, Chemical Shift, Absorption Edges, Electronegativity
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INTRODUCTION

Shifts to high energy of X-ray absorption edges are affected by two factors-

(i) the tighter binding of the core level because of the change of the effective charge (or screening) of the nucleus caused by the participation of the valence electron in the chemical-bond formation and (ii) the appearance of the energy gap going from metal to compound, which is related to phenomena such as covalence, effective charge, coordination number, crystal structure, etc. When bonding takes place, the shift in the X-ray absorption edge energy provides valuable information [1,2] on changes that occur in the conduction band. It is well known [3-7] that the chemistry of monovalent and trivalent thallium compounds derives from 6s and 6p electrons present in the valence band. The nature of the bonding in these compounds varies widely. Covalent contributions to the bonding [8] in thallium(I) halides are at maximum in thallous iodide, which has a double-layered orthorhombic structure [9]. Using known structural data, informative deductions on structure - bonding relations have been made. In this report, information complementary to Ref. 10 is provided.

ORIGIN OF DATA

The data were measured as described in Ref. 10. The thallium compounds used in these measurements were of high purity obtained from different sources. The absorber thickness was adjusted to give $I/I_0 = 1/3$ on the high absorption side of the edge.

RESULTS AND CONCLUSIONS

The results of the measurements on these compounds along with the values of electronegativity difference are given in Table 1.

1) The shift due to chemical combination is on the high energy side following Agarwal and Verma rule [11,12].

2) $Tl_2Ba_2O_5$ and $Tl_2Ta_2O_6$ wherein thallium has different oxidation states show different chemical shift. Similar trends were observed for nitrates and acetates. In compounds where thallium is present in the same oxidation state but bound to different ligands, the magnitudes of the observed shifts are different.

3) In all the superconducting oxides, the chemical shift is similar to that of Tl^{3+} compounds suggesting Tl^{3+} ions in these oxides.

4) The chemical shift decreases with decrease of electronegativity difference between the absorbing

TABLE 1. Chemical Shifts of L_{III} Absorption Edges of Thallium in its Compounds.

Sample No.	Absorber	Formal Valence	Bond Type	$\Delta\chi$	I%	Pauling's Ionic Charge[b] q	Chemical Shift[a] ΔE (eV)
1.	TlI	1	Tl - I	0.62	9.1	0.091	1.8
2.	TlBr	1	Tl -Br	0.92	19.1	0.191	2.5
3.	TlCl	1	Tl - Cl	1.12	26.9	0.269	2.8
4.	$Tl(CH_3COO)$	1	Tl - O	1.4	38.7	0.387	3.0
5.	$Tl_2Ta_2O_6$	1	Tl - O	1.4	38.7	0.387	3.1
6.	Tl_2CO_3	1	Tl - O	1.4	38.7	0.387	3.2
7.	$TlNO_3$	1	Tl - O	1.4	38.7	0.387	3.2
8.	$Tl\ (C_6H_5COCHCOCH_3)$	1	Tl - O	1.4	38.7	0.387	3.2
9.	Tl_2SO_4	1	Tl - O	1.4	38.7	0.387	3.3
10.	$Tl(C_5H_7O_2)$	1	Tl - O	1.4	38.7	0.387	3.3
11.	$Tl(CH_3COO)_3$	3	Tl - O	1.4	38.7	1.162	3.8
12.	$Tl\ (CF_3COO)_3$	3	Tl - O	1.4	38.7	1.162	3.9
13.	$Tl(NO_3)_3.3H_2O$	3	Tl - O	1.4	38.7	1.162	4.0
14.	$Tl_2Ba_2O_5$	3	Tl - O	1.4	38.7	1.162	4.0
15.	$Tl_2Ba_2CaCu_2O_8$	-	Tl - O	1.4	-	-	4.0
16.	$Tl_2Ba_2Ca_2Cu_3O_{10}$	-	Tl - O	1.4	-	-	4.0
17.	$TlBa_2CaCu_2O_7$	-	Tl - O	1.4	-	-	4.0
18.	$Tl_{0.5}Pb_{0.5}Sr_2CaCu_2O_7$	-	Tl - O	1.4	-	-	4.0
19.	$Tl_{0.8}V_{0.8}\ Sr_2(Ca_{0.8}Y_{0.2})Cu_2O_7$	-	Tl - O	1.4	-	-	4.0
20.	$Tl_{0.7}V_{0.7}Sr_2(Ca_{0.8}Y_{0.2})Cu_2O_7$	-	Tl - O	1.4	-	-	4.0
21.	$Tl_{0.6}V_{0.6}Sr_2(Ca_{0.8}Y_{0.2})Cu_2O_7$	-	Tl - O	1.4	-	-	4.0
22.	$Tl_{0.5}V_{0.5}Sr_2(Ca_{0.8}Y_{0.2})Cu_2O_7$	-	Tl - O	1.4	-	-	4.0

[a]Reference for Chemical Shift is taken as the position of thallium L_{III} Absorption Edge (12665 eV) in Tl_2O_3.
[b]For calculation of effective charge on thallium ions, the bonds in the first coordination cell of ligands around the thallium atom in all the model compounds and superconducting oxides are considered.

atom and its ligands. In the monovalent thallium compounds the electronegativity difference between thallium and chlorine is maximum for thallous chloride.

5) The edge shift depends on the magnitude of the final levels involved in the formation of chemical bonds and is mainly responsible for the observed chemical shifts.

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