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# X-ray photoelectron spectroscopic studies of the valence state of Tl in single-Tl-O-layered $TlBa_{1-x}Sr_xLaCuO_5$ ($0 \leq x \leq 1$)

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The valence state of thallium in $TlBa_{1-x}Sr_xLaCuO_5$ ($x = 0.0$, 0.4, 0.7, and 1.0) has been investigated by measuring Tl $4f$ core levels by x-ray photoelectron spectroscopy. It is shown that the valence state of Tl in $TlBaLaCuO_5$ (nonsuperconducting) is 3+, whereas that in $TlSrLaCuO_5$ (superconducting, $T_c = 32$ K) is between 3+ and 1+. The origin of holes in the latter compound is discussed in terms of charge transfer between Tl ions and Cu-O layers as has been found in double-Tl-O-layered compounds.

## I. INTRODUCTION

There are various mechanisms of generation of holes in $p$-type high-$T_c$ superconductors. Holes can be created by substitution of a higher-valence element by a lower-valence element as, for example, in $La_{2-x}Sr_xCuO_4$.[1] Excess of oxygen also leads to holes as in $YBa_2Cu_3O_{6+y}$ (Ref. 2) and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$.[3,4] Deficiency of oxygen in already overdoped single-Tl-O-layered compounds $TlA_2Ca_{n-1}Cu_nO_{2n+3}$ (Ref. 5) (where $A$=Ba,Sr) or charge-transfer, cation-vacancy, and/or order-disorder phenomena [as, for example, found in double-Tl-O-layered $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ (Refs. 6–9) compounds] also result in the creation of carriers.

The $TlBaLaCuO_5$ compound does not superconduct; it is, in fact, an insulator.[10] This is consistent with the fact that copper is in 2+ valence state and, chemically speaking, there are no carriers of electricity. However, the analogous system $TlSrLaCuO_5$ is a superconductor,[11] which is rather puzzling, since on chemical grounds this material should behave the same way as $TlBaLaCuO_5$. It has been suggested[12] that the origin of holes in $TlSrLaCuO_5$ could be due to charge transfer from Cu-O layers to Tl ions, just as in the case of double-Tl-O-layered compounds.[6] It is for this reason that we considered this to be of interest in obtaining a deeper insight into the origin of hole creation in $TlSrLaCuO_5$. Charge transfer should result in reduction of valence of Tl from 3+, which could be studied by x-ray photoemission spectroscopy (XPS). For this purpose we have prepared samples of $TlBa_{1-x}Sr_xLaCuO_5$ ($x$=0.0, 0.4, 0.7, and 1.0) and the results of our XPS measurements are described.

## II. EXPERIMENTAL DETAILS

The samples were prepared using the following procedure: Appropriate amounts of $Tl_2O_3$ (99.99%), $BaO_2$ (99.5%), $Sr_2CuO_3$ [prepared by solid-state reaction of $SrCO_3$ (99.99%) and CuO (99.99%) at 1000 °C for 3 days], $La_2O_3$ (99.99%), and CuO (99.99%) powders were mixed thoroughly and pelletized. The pellets were sintered at 880 °C in a sealed gold tube for 6 h and then furnace cooled to room temperature. The resultant products were reground and pelletized, and these pellets were annealed in flowing oxygen for various periods of time to get the highest $T_c$. The phase purity of the materials was checked by powder x-ray diffraction. The superconducting behavior of the samples was examined by the ac mutual inductance (frequency =313 Hz) technique. XPS measurements were carried out in ultrahigh vacuum of the order of $10^{-9}$ Torr using a VG Escalab MkII spectrometer equipped with a nonmonochromatized Mg $K\alpha$ x-ray ($h\nu = 1253.6$ eV) source, with an energy resolution better than 0.7 eV. The top few layers of the surface of the samples were scraped *in situ* with a steel blade. $Tl_2O_3$ was used as a standard for $Tl^{3+}$, while for $Tl^{+}$ the value of binding energy (BE) was taken from McGuire, Schweitzer, and Carlson.[13]

## III. RESULTS

An x-ray diffraction (XRD) pattern (Fig. 1) revealed that the samples are of single phase except for the presence of traces of $BaCO_3$ (as indicated by the line marked with an asterisk in the XRD patterns) in compounds with higher Ba content ($x=0.0$ and 0.4). All other lines could be indexed on the basis of the tetragonal 1:2:0:1 phase, with the space group *P4/mmm*. The lattice parameters $a$ and $c$ were obtained with a least-squares fitting procedure. Figure 2 shows the variation of the lattice parameters with $x$. Results of the ac susceptibility of the samples with $x=0.0$, 0.7, and 1.0 are shown in Fig. 3. The superconducting diamagnetic response was observed to be of comparable magnitude in all the samples studied. The superconducting transition temperature $T_c=20$, 30, and 32 K for $x=0.4$, 0.7, and 1.0, respectively. XPS spectra of Tl 4$f$ core levels of the samples were measured and are shown in Fig. 4. Core-level binding energies are referenced to the C 1$s$ peak at 284.9 eV.

## IV. DISCUSSION

### A. Structural aspects

While discussing the variation of the lattice parameters in systems such as $TlA_{2-x}La_xCuO_5$ (where $A=$Sr or Ba), one must consider the following two competing effects.

(i) The effect due to different sizes of the ions involved. On substituting bigger $A^{2+}$ ions (the radii of $Ba^{2+}$ and $Sr^{2+}$ ions are ~1.47 and ~1.31 Å, respectively, for ninefold coordination) by smaller $La^{3+}$ (radius ~1.21 Å for ninefold coordination[14]), one expects a decrease in both $a$ and $c$.

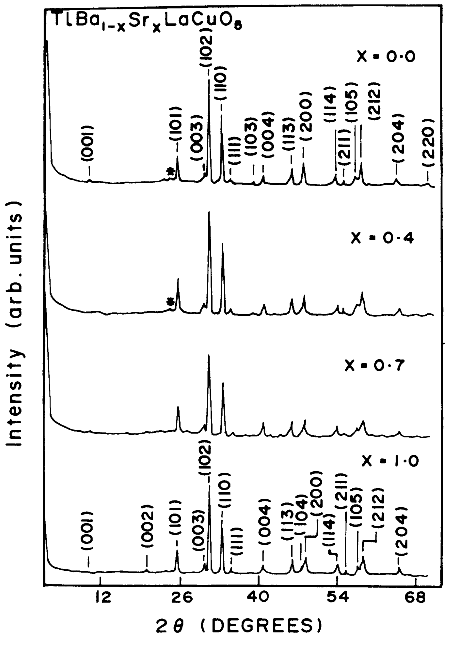

FIG. 1. X-ray powder diffraction pattern of $TlBa_{1-x}Sr_xLaCuO_5$ ($x=0.0$, 0.4, 0.7, and 1.0). The line marked with an asterisk indicates the presence of traces of $BaCO_3$. All the other lines can be indexed in terms of the 1:2:0:1 phase (space group *P4/mmm*).

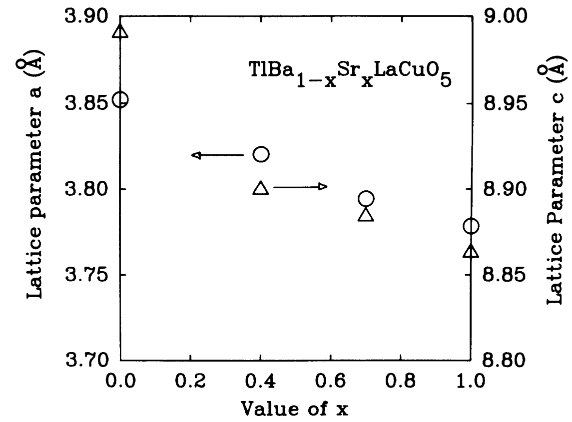

FIG. 2. Variation of lattice parameters $a$ (○) and $c$ (△) with $x$ in $TlBa_{1-x}Sr_xLaCuO_5$.

(ii) The effect due to the difference in the valence of the ions. Since the Cu-O bonds have antibonding character in the Cu-O layer ($d_{x^2-y^2}$ bands[15,16]), substitution of divalent Sr (Ba) ions by trivalent $La^{3+}$ ions introduces an extra electron, which is accommodated in the Cu-O layers, thereby reducing the Cu valence. This should result in an increase in the in-plane Cu-O bond length. This effect increases primarily $a$ because, in general, the in-plane Cu-O bond length ($r_{Cu\text{-}O}$), in single- and double-Tl-O-layered compounds is close to one-half of the lattice parameter $a$.

In the case of $A=$Sr, the second effect outweighs the first one, resulting in a slight increase[11] of $a$. In the case of $A=$Ba, the first effect is more important because of the large difference in the sizes of the ions involved.[17]

In $TlBa_{1-x}Sr_xLaCuO_5$, which are of interest in the present investigation, a large decrease of $a$ (Fig. 2) arises mainly because of the overlap of Tl 6$s$ bands and Cu

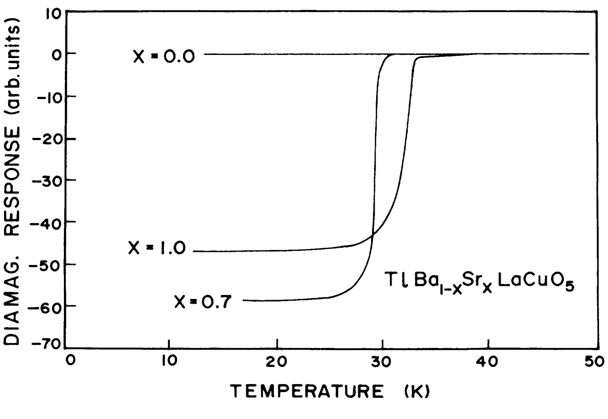

FIG. 3. Diamagnetic response as a function of temperature in $TlBa_{1-x}Sr_xLaCuO_5$ ($x=0.0$, 0.7, and 1.0).

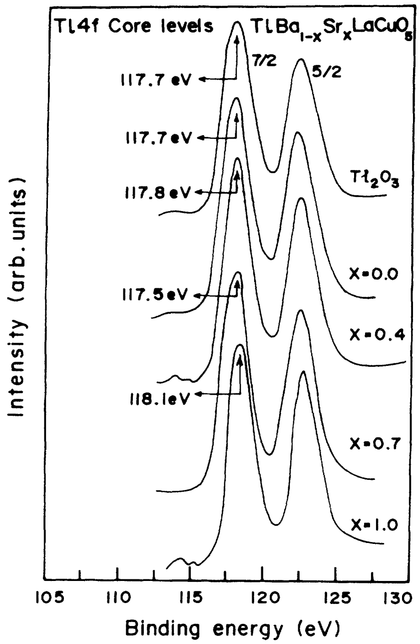

FIG. 4. XPS spectra of Tl 4$f$ core levels of $Tl_2O_3$ and $TlBa_{1-x}Sr_xLaCuO_5$ ($x=0.0$, 0.4, 0.7, and 1.0). Binding energies are referenced to the C 1$s$ peak at 284.9 eV.

$3d_{x^2-y^2}$ bands. Because of this overlap, electrons from Cu ions are emptied onto Tl ions, creating holes in the Cu-O layers. This results in shortening of the in-plane Cu-O bond length (thereby decreasing $a$). This is in addition to the above-mentioned ionic-size effect.

### B. XPS of the Tl $4f_{7/2}$ level

XPS of Tl $4f_{7/2}$ core levels has been studied by McGuire, Schweitzer, and Carlson[13] in $Tl_2O_3$ and some Tl(I) compounds. The BE of the $4f_{7/2}$ level in Tl(I) compounds was observed to be higher (the BE varies between 118.7 and 119.4 eV, depending on the ligands) than that of $Tl_2O_3$ (BE = 117.7 eV). Our XPS results of the binding energy of Tl $4f_{7/2}$ in $Tl_2O_3$ are consistent with those of McGuire, Schweitzer, and Carlson. The BE of the $4f_{7/2}$ core level, as mentioned in the present work (see Fig. 4), in the compounds with $x=0.0$, 0.4, 0.7, and 1, respectively, is 117.7, 117.8, 117.9, and 118.1 eV. Since the nearest-neighbor environment of Tl atoms remains essentially the same in these materials, we interpet the variation of the BE, as also observed in double-Tl-O-layered compounds,[18–20] to be suggesting a shift of valence of Tl ions from 3+ to 1+. These results support theoretical band calculations recently reported by Whangbo and Subramanian.[12]

We carried out XPS studies of Tl 4$f$ core levels in two similar materials, namely, superconducting $TlBa_{1.2}La_{0.8}CuO_5$ ($T_c=32$ K) and nonsuperconducting $TlBa_{1.2}La_{0.8}CuO_{5-y}$ (oxygen deficient). The method of preparation of these materials has already been described elsewhere.[17] It is, however, relevant to point out here that the nonsuperconducting material could be made superconducting by appropriate oxygen annealing. This process could be carried out reversibly.

The valence state of Tl in superconducting $TlBa_{1.2}La_{0.8}CuO_5$ is 3+, as inferred from the observed BE (117.7 eV) of the $4f_{7/2}$ level of Tl. Simple electron counting implies that the average valence of Cu is $\sim +2.2$. This nonintegral valence of copper, responsible for the generation of holes in this system, comes about by introducing excess oxygen, just as in many other high-$T_c$ materials. This observation reveals that in the same family of compounds $TlA_2CuO_5$ (where $A$ = Ba or Sr), depending upon the chemical (and the accompanying structural) changes, different mechanisms operate to generate holes. In $TlSrLaCuO_5$, holes are generated via the charge transfer from Cu ions to Tl ions, whereas in $TlBa_{1.2}La_{0.8}CuO_5$ it is the oxidation of Cu ions from 2+ to a higher-valence state, without affecting the Tl valence, that generates holes.

The Tl valence in nonsuperconducting $TlBa_{1.2}La_{0.8}CuO_{5-y}$ is inferred to be intermediate between 3+ and 1+ (BE of the $4f_{7/2}$ level of Tl = 118.0 eV), suggesting that Tl ions are reduced or oxidized by varying the oxygen stoichiometry of the material.

## V. CONCLUSION

We have reported results of XPS measurements on $TlBa_{1-x}Sr_xLaCuO_5$. These studies suggest that as $x$ increases, the BE of the $4f_{7/2}$ level of Tl also increases. This is a clear evidence of the valence of Tl changing toward $Tl^+$. The process of the internal redox mechanism, because of the overlap of the Tl 6$s$ and Cu $3d_{x^2-y^2}$ block bands is responsible for generating carriers in $TlSrLaCuO_5$. On the other hand, hole carriers in $TlBa_{2-x}La_xCuO_{5-y}$ are produced by varying the oxygen stoichiometry. It would be instructive to study the effect of the internal reduction of Tl ions in $TlSrLaCuO_5$ by other techniques such as NMR. These efforts are underway.

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