

Superconductivity and valence state of Tl in $\text{TlA}_{2-x}\text{La}_x\text{CuO}_5$ and $\text{TlA}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_7$ ($A = \text{Ba, Sr}$)

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Our x-ray core-level spectroscopic measurements show that the valence state of Tl in Ba containing single-Tl-O-layered compounds $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ and $\text{TlBa}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_7$ is +3 whereas in Sr containing single-Tl-O-layered compounds $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$ and $\text{TlSr}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_7$ is between +3 and +1. The origin of holes in the latter is discussed in terms of charge transfer between the Tl 6s band and the Cu $3d_{x^2-y^2}$ band in addition to the holes generated due to excess oxygen. This is in contrast to the former wherein the origin of the holes is due to the excess of oxygen only.

I. INTRODUCTION

Holes in double-Tl-O-layered high- T_c superconductors (hereafter referred to as Tl-2) $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n = 1-4$) are generated mainly by overlap of the empty Tl 6s band with antibonding of the Cu $3d_{x^2-y^2}$ bands at the Fermi level.¹⁻³ Single-Tl-O-layered compounds $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ ($n = 1-5$), to be called TlBa-1, are overdoped, optimally doped, or underdoped depending upon the number n of the CuO_2 layers, except for $n = 1$. This is because excess oxygen, according to the above formula, depends on n , the number of neighboring CuO_2 layers.^{4,5} In the case of $n = 1$, the copper must be present in the +3 oxidation state and is not expected to superconduct. In fact, synthesis of this material as a single phase is very difficult. In Tl-2 compounds, there are eight Tl-Tl nearest-neighbor ions which make the Tl 6s band broader in comparison to that in Tl-1 compounds in which case there are only four Tl-Tl nearest-neighbor ions per primitive cell (see Fig. 1). As a result, the empty Tl 6s band in Tl-2 compounds lies below the Fermi level, in contrast to Tl-1 compounds where it lies above the Fermi level, and overlaps with a lower Hubbard band of Cu $3d_{x^2-y^2}$ band. This leads to the creation of holes in the latter and an increase in the electron density in the former. As a consequence, there is a reduction of the Tl valence from +3.⁶ The Tl 6s band in TlBa-1 compounds does not overlap with the Cu $3d_{x^2-y^2}$ band. Thus the holes are generated due to excess oxygen, the valence state of Tl remaining +3.⁷

There is yet another series of single-Tl-O-layered compounds namely, $\text{TlSr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ (Refs. 8-10) to be called TlSr-1. They are isostructural with TlBa-1 compounds, n being 1, 2, and 3 only. Materials belonging to these two series differ in their superconducting properties. For example, TlBaLaCuO_5 (TlBa-1:2:0:1) is a semiconductor¹¹ whereas the isostructural compound TlSrLaCuO_5 (TlSr-1:2:0:1) is a superconductor.¹² In the second member of the TlSr-1 series, $\text{TlSr}_2\text{CaCu}_2\text{O}_7$ (Ref. 13) (TlSr-1:2:1:2) the superconductivity is retained for relatively higher value of rare-earth substitution at the 8-

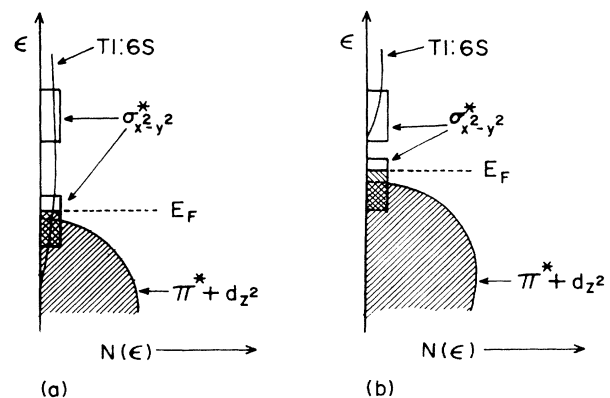


FIG. 1. Energy density of states $N(\epsilon)$ versus energy ϵ for (a) $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ and (b) $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$.

coordinated Ca site or 9-coordinated Sr site compared to that in the TlBa-1 series.¹⁴ It had been suggested theoretically,¹⁵ and shown experimentally by x-ray-photoelectron spectroscopic (XPS) measurements that the origin of holes in TlSrLaCuO₅ is due to the overlap of the Tl 6s band with the Cu 3d_{x²-y²} band.⁷ We suspected that this mechanism may be operative in the TlSr-1:2:1:2 also. In order to understand the origin of holes in TlA₂Ca_{n-1}Cu_nO_{2n+3} (A = Ba, Sr; n = 1, 2), and the difference in superconducting behavior between TlBa_{2-x}La_xCuO₅ and TlSr_{2-x}La_xCuO₅, TlBa₂Ca_{1-x}Gd_xCu₂O₇ and TlSr₂Ca_{1-x}Gd_xCu₂O₇, we undertook XPS investigations on these materials. This paper reports the results of these studies.

II. EXPERIMENTAL

The method of preparation of TlA_{2-x}La_xCuO₅ and Tl(A)₂Ca_{1-x}Gd_xCu₂O₇ (A = Ba, Sr) with various values of x has been described elsewhere,⁷ except that the sintering temperature for Tl-1:2:1:2 was 900 °C. All the samples were annealed in oxygen after presintering. Phase purity of the samples was checked by powder x-ray-diffraction (XRD) with a JEOL 8030 x-ray diffractometer using Cu Kα radiation (within the resolution of the instrument, typically a few percent). The superconducting property was studied by dc-electrical resistance measurements. The valence state of thallium was studied by x-ray core-level photoelectron spectroscopy measurements under ultrahigh vacuum (~10⁻⁹ Torr) using a VG Escalab MkII spectrometer equipped with a nonmonochromatized Mg Kα x-ray (hν = 1253.6 eV) source. Energy resolution of the instrument was better than 0.7 eV which is relative to metallic silver.^{16,17} Binding-energy (BE) values were obtained from the peak position after subtracting the background linearly. The uncertainty in determining the BE values is ±0.1 eV. Since these samples have well-known surface contamination problems, we have taken maximum care to minimize the effects by scraping the sample thoroughly over the surface with a stainless steel blade *in situ* under ultrahigh vacuum. Before scraping, these samples showed a high intense C 1s peak at BE = 289 eV and a double-peak structure for O 1s with BE in the range 528–532 eV. After scraping the surface of the material thoroughly, no C 1s peak was observed and only one O 1s peak was observed at 528.7 eV showing the absence of carbonate impurities. The Tl 4f core-level spectra were recorded after scraping. Silver paint was used to minimize the charging. However, the metallic samples did not show any charging.

In order to measure the BE of instrumental C 1s, in the absence of carbonate impurity, the samples were allowed in the vacuum chamber for 2–3 h to accumulate the instrumental carbon over the sample surface. The BE value of the C 1s peak was determined to be 285.0 eV. BE values of the samples are referenced to this value. Tl₂O₃ was used as a standard for Tl³⁺, while for Tl⁺ the values of BE was taken from McGuire, Schweitzer, and Carlson.¹⁸

III. RESULTS AND DISCUSSION

A. TlBa_{2-x}La_xCuO₅ and TlSr_{2-x}La_xCuO₅ (0.0 ≤ x ≤ 1.0)

Structure and superconductivity

XRD patterns of TlBa_{2-x}La_xCuO₅ and TlSr_{2-x}La_xCuO₅ showed that the samples with 0.2 ≤ x ≤ 1.0 and 0.6 ≤ x ≤ 1.0, respectively, are single phase. The spectra of Ba-containing samples, however, indicated the presence of traces of BaCO₃ impurity which basically are confined to the surface of the sample. Our XPS spectra (as discussed in experimental) do suggest that BaCO₃ is present only at the surface of the material. All the other diffraction lines could be indexed on the basis of tetragonal 1:2:0:1 phase, (space group P4/mmm). The lattice parameters a and c, obtained from least-square fitting procedure, in both TlBa_{2-x}La_xCuO₅ and TlSr_{2-x}La_xCuO₅ are plotted as a function of x in Figs. 2 and 3, respectively. While discussing the variation of a with La³⁺ concentration in TlA_{2-x}La_xCuO₅ (A = Ba, Sr) one should consider the following two competing effects. (i) *Ionic size effect*, the effect due to different sizes of the ions involved: On substituting bigger A²⁺ ions (the radii of Ba²⁺ and Sr²⁺ ions are ~1.47 and ~1.31 Å, respectively, for ninefold coordination) by smaller La³⁺ ions (radius ~1.21 Å for ninefold coordination¹⁹), one expects a decrease in both a and c. (ii) *Valence effect*, the effect due to the difference in the valence of the ions: Since the Cu-O bonds have antibonding character in the CuO₂ layer (d_{x²-y²} bands²⁰), substitution of divalent Ba(Sr) ions by trivalent La³⁺ ions introduces an extra electron, which is accommodated in the CuO₂ layers, thereby reducing the Cu valence. This should result in an increase in the in-plane bond length r_{Cu-O}. This effect increases primarily a because, in general, the inplane r_{Cu-O} in single- and double-Tl-O-layered compounds is close to one-half of the lattice parameter a.

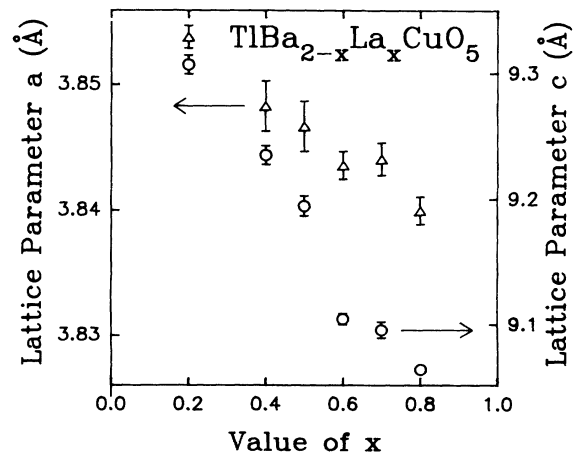


FIG. 2. Variation of lattice parameters a (Δ) and c (○) with x in TlBa_{2-x}La_xCuO₅. Both the lattice parameters decrease with increase of x. This is consistent with the ionic size effect (see text).

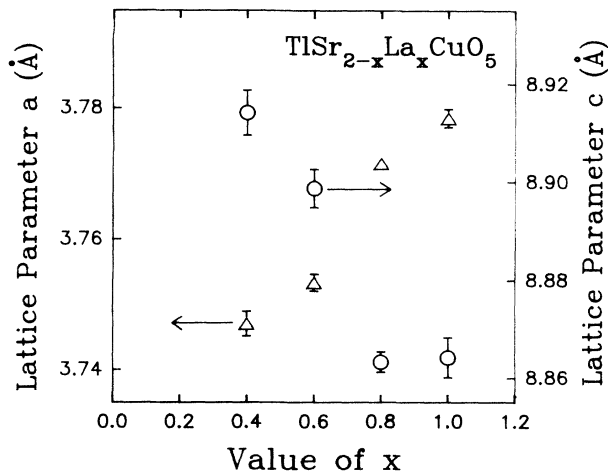


FIG. 3. Variation of lattice parameters a (Δ) and c (\circ) with x in $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$. The parameter a increases whereas c decreases with increase of x because of the valence and ionic size effects, respectively.

In the case of $A = \text{Ba}$, the ionic size effect is more important because of the large differences in the sizes of the ions involved. In the case of $A = \text{Sr}$, the valence effect outweighs the first effect, resulting in a slight increase of a .

Electrical resistance measurements show that the materials $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ and $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$ superconduct for x in the range $0.4 \leq x \leq 0.9$ and $0.8 \leq x \leq 1.0$, respectively. Superconducting transition temperature T_c in the system $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ is plotted as a function of x in Fig. 4. Samples with $x = 0.2$ in $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ and $x = 0.6$ in $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$ show metallic behavior and a broad drop in resistance, but did not reach a zero resistance state down to 12 K. This implies that the materials are overdoped with holes. From Fig. 4, it is clear that the variation of T_c with x in $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ is similar to what has been observed in other high- T_c materials, for

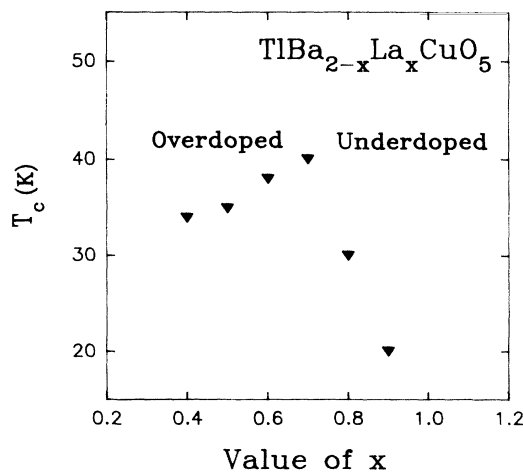


FIG. 4. Variation of T_c with x in $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$. Materials in the range $0.4 \leq x < 0.7$ and $0.7 < x \leq 0.9$ are overdoped and underdoped with holes, respectively.

example in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.²¹ Materials in the range $0.2 \leq x < 0.7$ and $0.7 < x \leq 0.9$ are, respectively, overdoped and underdoped with holes. It is important to note that in the case of $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$, only samples with $x = 0.8$ and 1.0 superconduct with $T_c = 27$ and 32 K, respectively. Metallic behavior of resistance with temperature and variation of T_c with x show that the system $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$ with $0.6 \leq x < 1.0$ is in the overdoped state.

XPS of Tl $4f_{7/2}$ core level in $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ and $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$ ($x = 0.6, 0.8, \text{ and } 1.0$)

The XPS of Tl $4f_{7/2}$ core-level BE in Tl_2O_3 is 117.7 eV which is consistent with the reported value.¹⁶ The BE of the Tl $4f_{7/2}$ core level is 117.7 eV for $x = 0.6, 0.8, \text{ and } 1.0$ in $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$. This value is in good agreement with the value of 117.7 eV for Tl $4f_{7/2}$ in Tl_2O_3 . This suggests that the valence state of Tl in superconducting $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ ($x = 0.6$ and 0.8) and nonsuperconducting $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$ ($x = 1.0$) is +3. This implies that the Tl $6s$ band lies above the Fermi level and thus does not remove electrons from the $\text{Cu } 3d_{x^2-y^2}$ band. Thus the holes are generated owing to the excess oxygen only. These results provide support to the calculations of electronic band structure in $\text{TlBa}_2\text{CuO}_5$.¹

XPS of Tl $4f_{7/2}$ in $\text{TlSr}_{2-x}\text{La}_x\text{CuO}_5$ ($x = 0.6, 0.8, \text{ and } 1.0$) is shown in Fig. 5. As can be seen from the figure, the BE of the Tl $4f_{7/2}$ core level in these compounds has moved up (BE = 118.3, 118.2, and 118.1 eV for $x = 0.6, 0.8, \text{ and } 1.0$, respectively) suggesting that, the valence state of Tl is between +3 and +1 as the near-neighbor environment of Tl ions remains essentially the same in these materials. Decrease of BE with an increase of the concentration of La^{3+} ions is consistent with the fact that the addition of an extra electron, contributed by lanthanum ion, into the band of the antibonding $\text{Cu } 3d_{x^2-y^2}$ orbitals could result in a decrease of effective overlap of the Tl $6s$ band with the $\text{Cu } 3d_{x^2-y^2}$ band and hence the decrease in electron density in the Tl $6s$ band. From the chemical bonding considerations, addition of electrons into the antibonding band increases the in-plane Cu-O bond length $r_{\text{Cu-O}}$. This is clearly reflected in the lattice parameter a which increases with the increase of concentration of La^{3+} ions. This situation is to be contrasted with that in the system $\text{TlBa}_{1-x}\text{Sr}_x\text{LaCuO}_5$.⁷ In this system, an increase of BE and T_c with the increase of isovalent Sr^{2+} ion concentration reveals that this system moves from being underdoped ($x > 0.4$) to being optimally doped.

B. $\text{TlBa}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_7$ ($x = 0.3$ and 1.0) and $\text{TlSr}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_7$ ($x = 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$)

Structure and superconductivity

XRD patterns of $\text{TlBa}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_7$ ($x = 0.3$ and 1.0) show the single-phase (tetragonal 1:2:1:2 phase with the space group $P4/mmm$) nature of the materials except

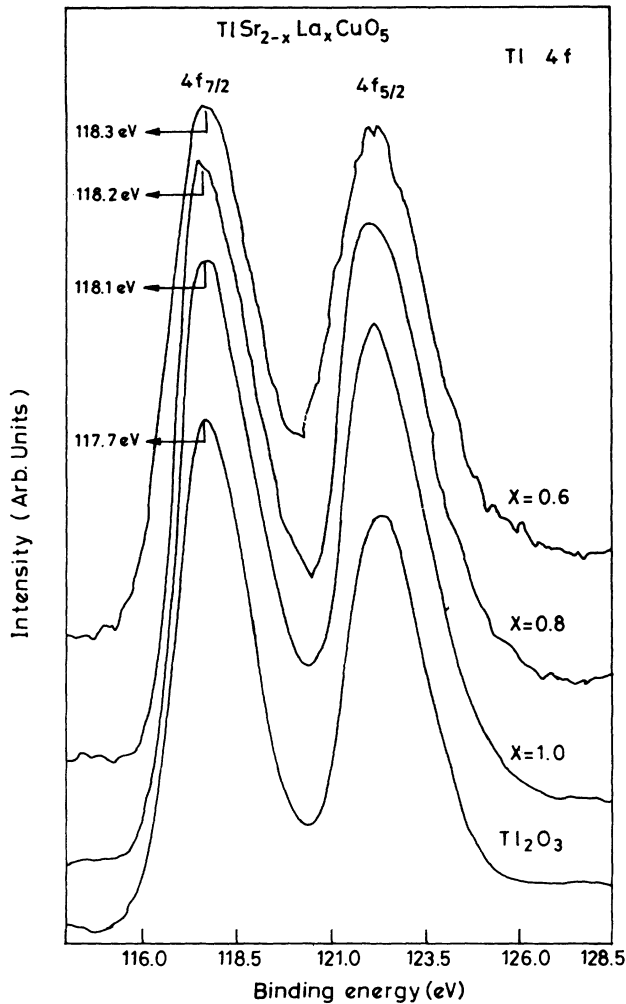


FIG. 5. XPS spectra of Tl $4f_{7/2}$ core levels in Tl_2O_3 and $TlSr_{2-x}La_xCuO_5$ ($x=0.6, 0.8, \text{ and } 1.0$). Binding energies are referenced to the instrumental $C 1s$ peak at 285 eV.

a trace of $BaCuO_2$ impurity phase for $x=0.3$. Single-phase samples could be obtained for $0.4 \leq x \leq 1.0$ in $TlSr_2Ca_{1-x}Gd_xCu_2O_7$ except the presence of traces of an impurity for $x=0.4$. Lattice parameters for both systems are listed in Table I. It should be noted that in both systems, lattice parameter a increases, whereas parameter c decreases, with increase of x . This is because, the variation of the a parameter is primarily due to the *valence effect* (mentioned above) and the decrease of the c param-

TABLE I. Compounds and their corresponding lattice parameters a and c , T_c and BE of Tl $4f_{7/2}$ core level [nonsuperconducting (NSC)].

Compound	a (Å)	c (Å)	T_c (K)	BE of Tl- $4f_{7/2}$ (eV)
$TlSr_2Ca_{0.6}Gd_{0.4}Cu_2O_7$	3.808	12.081	65	
$TlSr_2Ca_{0.4}Gd_{0.6}Cu_2O_7$	3.816	12.046	60	118.3
$TlSr_2Ca_{0.2}Gd_{0.8}Cu_2O_7$	3.828	12.047	NSC	118.2
$TlSr_2GdCu_2O_7$	3.833	12.021	NSC	118.1
$TlBa_2Ca_{0.7}Gd_{0.3}Cu_2O_7$	3.867	12.601	78	117.7
$TlBa_2GdCu_2O_7$	3.899	12.296	NSC	117.7

eter is due to the substitution of bigger Ca^{2+} ions by smaller Gd^{3+} ions, the *ionic size effect*. Resistance measurements show that the compound $TlBa_2Ca_{1-x}Gd_xCu_2O_7$, $x=0.3$, superconducts with $T_c=78$ K. The compound with $x=1.0$ is a semiconductor. In the case of the system $TlSr_2Ca_{1-x}Gd_xCu_2O_7$ the compounds with $x=0.4$ and 0.6 superconduct with $T_c=65$ and 60 K, respectively. Compounds with $x=0.8$ do not superconduct down to 12 K and $x=1.0$ is a semiconductor just as $TlBa_2GdCu_2O_7$.

*XPS of Tl $4f_{7/2}$ core level
in $TlBa_2Ca_{1-x}Gd_xCu_2O_7$ ($x=0.3$ and 1.0)
and $TlSr_2Ca_{1-x}Gd_xCu_2O_7$ ($x=0.6, 0.8, \text{ and } 1.0$)*

The BE of the Tl $4f_{7/2}$ core level in $TlBa_2Ca_{1-x}Gd_xCu_2O_7$ with $x=0.3$ and 1.0 is listed in Table I. The BE of Tl $4f_{7/2}$ in superconducting $TlBa_2Ca_{0.7}Gd_{0.3}Cu_2O_7$ and nonsuperconducting $TlBa_2GdCu_2O_7$ is 117.7 eV. This value implies that the valence state of Tl in these compounds is $+3$, in agreement with electronic band-structure calculations and high-energy spectroscopic studies.^{1,2} The BE of Tl $4f_{7/2}$ in $TlSr_2Ca_{1-x}Gd_xCu_2O_7$ is also listed in Table I. The BE of Tl $4f_{7/2}$ in samples with $x=0.6, 0.8, \text{ and } 1.0$, respectively is $118.3, 118.2, \text{ and } 118.1$ eV suggesting that the valence of Tl is systematically moving towards $+3$. This suggests that the system $TlSr_2GdCu_2O_7$, just like $TlSr_2CuO_5$, has more Cu^{3+} content because of the holes generated due to overlap of Tl $6s$ band with Cu $3d_{x^2-y^2}$ band in addition to those generated due to excess oxygen. Decrease of BE and T_c with x suggests that the system $TlSr_2Ca_{1-x}Gd_xCu_2O_7$ with $x(>0.4)$ moves towards being underdoped. In this respect, this material is different from the system $TlSr_{2-x}La_xCuO_5$, although the BE values are similar and vary in a similar fashion. $TlSrLaCuO_5$ with a BE of 118.1 eV is a superconductor, whereas $TlSr_2GdCu_2O_7$ with the same BE is not a superconductor. This is because in the system $TlSr_2Ca_{1-x}Gd_xCu_2O_7$, holes which are generated by the redox mechanism are divided between two CuO_2 layers whereas in $TlSr_{2-x}La_xCuO_5$ the holes belong to only one CuO_2 layer. In $TlSr-1:2:0:1$ and $TlSr-1:2:1:2$ systems the redox mechanism becomes effective because of relatively smaller lattice parameter compared with, respectively, isostructural $TlBa-1:2:0:1$ and $TlBa-1:2:1:2$ materials. In the case of Tl-2 compounds it is due to the higher number (eight) of Tl-Tl nearest-neighbor interaction, as mentioned above, compared to single-Tl-O-layered compounds where there are only four Tl-Tl nearest neighbors.

IV. CONCLUSION

The XPS of Tl $4f_{7/2}$ in single-Tl-O-layered $TlSr_{2-x}La_xCuO_5$ and $TlSr_2Ca_{1-x}Gd_xCu_2O_7$ show that the valence state of Tl is between $+3$ and $+1$, implying that holes are generated due to the redox mechanism also in addition to the holes being generated due to excess oxygen. Our measurement on the isostructural $TlBa_{2-x}La_xCuO_5$ and $TlBa_2Ca_{1-x}Gd_xCu_2O_7$ systems show that the Tl valence is essentially $+3$. Thus elec-

trons are not transferred from CuO_2 layers into the Tl 6s band in these two systems. Smaller values of lattice parameters in TlSr-1:2:0:1 and TlSr-1:2:1:2 compared to that in TlBa-1:2:0:1 and TlBa-1:2:1:2 are responsible for the presence of the redox mechanism of hole generation.

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