

# Possible overdoping in $\text{TlSrLaCuO}_5$ and superconductivity in $\text{TlBaLaCuO}_5$ by isovalent-cation substitution

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It is known that superconductivity in  $\text{TlSrLaCuO}_5$  is due to the overlap of empty Tl 6s band with the antibonding Cu  $3d_{x^2-y^2}$  band at the Fermi level. This motivated us to investigate the effects of isovalent-cation substitution in superconducting  $\text{TlSrLaCuO}_5$  and semiconducting  $\text{TlBaLaCuO}_5$ . We have succeeded in inducing superconductivity in  $\text{TlBaLaCuO}_5$  by introducing  $\text{Ca}^{2+}$  at the Ba sites.

## I. INTRODUCTION

Holes in single Tl-O layered compounds  $\text{TlA}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  (where  $A = \text{Ba}$  or  $\text{Sr}$  and  $n = 1-5$ ) and double Tl-O layered compounds  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  (where  $n = 1-4$ ) are created via two different mechanisms.<sup>1,2</sup> In the former class, itinerant charge carriers are created either by introducing higher-valence cations<sup>2-4</sup> in place of lower-valence cations or by creating anion nonstoichiometry.<sup>5</sup> In the latter class, holes are largely created by the preexisting redox mechanism,<sup>6,7</sup> i.e., due to the overlap of the empty Tl 6s band with the antibonding Cu  $3d_{x^2-y^2}$  band [see Fig. 1(a)], electrons are transferred from  $\text{CuO}_2$  planes to Tl-O layers and vice versa:  $\text{Tl}^{3+} + \text{Cu}^{2+} \rightleftharpoons \text{Tl}^{(3-\delta)+} + \text{Cu}^{(2+\delta)+}$ . Recently, it has been proposed that the redox mechanism is responsible for hole generation in a derivative of the single Tl-O layered compound with  $n = 1$ ,  $\text{TlSrLaCuO}_5$  ( $T_c = 32$  K). This conclusion follows from tight-binding electronic band-structure calculations<sup>8</sup> and has been established experimentally by x-ray-photoelectron spectroscopic studies on  $\text{TlBa}_{1-x}\text{Sr}_x\text{LaCuO}_5$ .<sup>9</sup> It should be pointed out that the isostructural compound  $\text{TlBaLaCuO}_5$  is not a superconductor, in fact it is a semiconductor.<sup>3</sup> In this case, the Fermi level lies below the bottom of the Tl 6s band, as shown in Fig. 1(b), rendering the redox mechanism non-operative.<sup>10</sup>

In order to make the redox mechanism in  $\text{TlBaLaCuO}_5$  operative, the lower Cu  $3d_{x^2-y^2}$  Hubbard band must be raised (in energy) so as to overlap with the empty Tl 6s band. This is possible if one is able to decrease the in-plane Cu-O bond length. As the Cu-O bond length decreases, the Fermi level rises and moves toward the empty Tl 6s band. Eventually, the Cu  $3d_{x^2-y^2}$  band overlaps

with the Tl 6s band [see Fig. 1(c)]. This causes electrons to flow from Cu ions to Tl ions and holes are introduced in the Cu band.

Experimentally, a decrease of the Cu-O bond length may be accomplished by substituting the bigger  $\text{Ba}^{2+}$  ions in  $\text{TlBaLaCuO}_5$  with smaller isovalent cations,<sup>9,11</sup> for example,  $\text{Sr}^{2+}$ . Both the lattice parameters  $a$  and  $c$  of the tetragonal structure of the system  $\text{TlBa}_{1-x}\text{Sr}_x\text{LaCuO}_5$  decrease as a function of  $x$ . The decrease in  $a$  implies a decrease of the in-plane Cu-O bond length because it has been observed that in all thallium-based high- $T_c$  superconductors the in-plane Cu-O bond length is one-half of  $a$ . The concentration of holes may be increased by increasing  $x$  in  $\text{TlBa}_{1-x}\text{Sr}_x\text{LaCuO}_5$ . As a

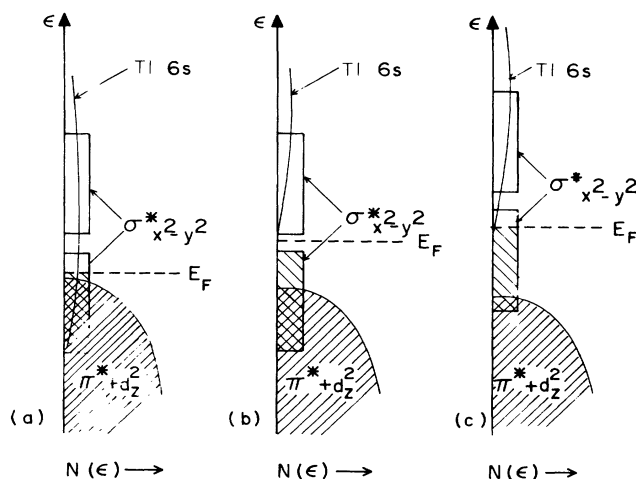


FIG. 1. Energy density of states  $N(\epsilon)$  vs energy  $\epsilon$  for nominal (a)  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ , (b)  $\text{TlBaLaCuO}_5$ , and (c)  $\text{TlSrLaCuO}_5$ . [(a) and (c) adapted from Ref. 10].

result,  $T_c$  also increases. Interestingly, the maximum  $T_c$  is observed in  $\text{TlSrLaCuO}_5$  (32–46 K depending upon the preparative conditions<sup>9,12,13</sup>). One may expect that the hole concentration in  $\text{TlSrLaCuO}_5$  may increase (leading to overdoping of holes) if the degree of overlap is further increased by substituting  $\text{Sr}^{2+}$  ions by still smaller isovalent cations ( $\text{Ca}^{2+}$ ). This should induce a variation of  $T_c$  ( $T_c$  should further increase, or if the compound is already optimally hole doped  $T_c$  should decrease due to overdoping) in the system  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$  in a manner similar to that in other high- $T_c$  superconductors, such as  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .<sup>14</sup> These considerations led us to examine the effect of hole doping in  $\text{TlBaLaCuO}_5$  by introducing the smaller  $\text{Ca}^{2+}$  ions. We have, in fact, succeeded in inducing superconductivity in this material following this approach. In this paper, we report the results of these investigations.

## II. EXPERIMENTAL

Samples of the type  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$  ( $0 \leq y \leq 1.0$ ) and  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  ( $0 \leq z \leq 1.0$ ) were prepared by the method followed in our preparation of the materials  $\text{TlBa}_{1-x}\text{Sr}_x\text{LaCuO}_5$ .<sup>9</sup> The phase purity of the samples was checked by x-ray powder diffraction. The superconducting properties were examined by the ac mutual inductance (frequency = 313 Hz) technique and four-probe resistance measurements. In order to check reproducibility of the results, three independent batches of the above-mentioned samples were made and investigated.

## III. RESULTS

X-ray powder diffraction (XRD) showed that essentially single-phase samples of the composition  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$  are formed for  $0.0 \leq y \leq 0.6$  and of the composition  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  for  $0.0 \leq z \leq 0.8$ . The powder-diffraction pattern of  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  ( $z = 0.0-0.8$ ) is shown in Fig. 2. Traces of some impurity phases in materials of both systems were seen. Diffraction lines could be indexed on the basis of the 1:2:0:1 phase, with the space group  $P4/mmm$ . Lattice parameters  $a$  and  $c$ , obtained using a least-squares fitting procedure, are given in Table I. ac susceptibility measurements of two samples of the system  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$ , namely, those corresponding to  $y = 0.3$  and  $0.6$ , showed that the superconducting onset temperature, respectively, is 32 and 26 K. Figure 3 shows the normalized resistance of these samples as a function of temperature. Zero-resistance temperatures  $T_{c0}$  for the two samples are 30 and 20 K, respectively.

Superconductivity was observed in the system  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  with  $12 < T_c < 16$  K for  $0.3 \leq z \leq 0.8$ . Figure 4 shows the resistance of the material  $\text{TlBa}_{0.4}\text{Ca}_{0.6}\text{LaCuO}_5$  as a function of temperature;  $T_{c0} = 13$  K. The inset of Fig. 4 shows the diamagnetic response of this material as a function of temperature, with onset temperature  $\sim 16$  K. In view of the fact that the effect of Ca doping in  $\text{TlBaLaCuO}_5$  is of particular interest, we synthesized two independent samples of

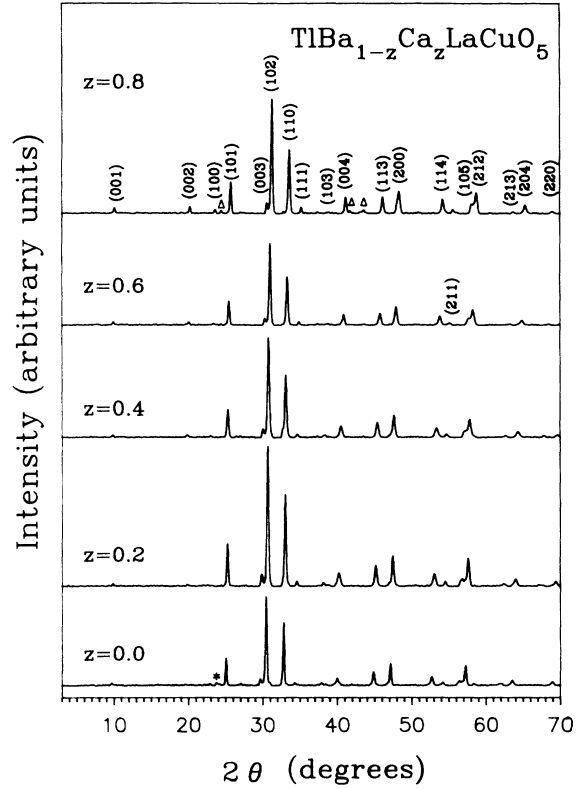


FIG. 2. X-ray powder-diffraction pattern of  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  ( $z = 0.0, 0.2, 0.4, 0.6$ , and  $0.8$ ). The lines marked (\*) and ( $\Delta$ ) indicate the presence of traces of  $\text{BaCO}_3$  (only in the higher-Ba-content samples) and  $\text{La}_2\text{CuO}_4$  (only in the higher-Ca-content sample), respectively. All the other lines can be indexed in terms of the 1:2:0:1 phase (space group  $P4/mmm$ ).

$\text{TlBa}_{0.4}\text{Ca}_{0.6}\text{LaCuO}_5$  and both the samples gave similar results. The strength of the ac  $\chi$  signal at the lowest temperature of our measurements (4.2 K) suggests clearly the  $\text{TlBa}_{0.4}\text{Ca}_{0.6}\text{LaCuO}_5$  is a bulk superconductor (the superconducting volume fraction is estimated to be in excess of 60%).

TABLE I. Compounds and their corresponding lattice parameters  $a$  and  $c$ , tolerance factor  $t$ , and diamagnetic onset temperature.

Compound	$a$ (Å)	$c$ (Å)	$t$	$T_c$ (K)
$\text{TlBaLaCuO}_5$	3.852	8.9928	0.860	
$\text{TlBa}_{0.6}\text{Sr}_{0.4}\text{LaCuO}_5$	3.821	8.901	0.852	20
$\text{TlBa}_{0.3}\text{Sr}_{0.7}\text{LaCuO}_5$	3.794	8.885	0.848	30
$\text{TlSrLaCuO}_5$	3.779	8.864	0.842	32
$\text{TlSr}_{0.7}\text{Ca}_{0.3}\text{LaCuO}_5$	3.761	8.807	0.838	32
$\text{TlSr}_{0.4}\text{Ca}_{0.6}\text{LaCuO}_5$	3.753	8.737	0.834	26
$\text{TlBa}_{0.8}\text{Ca}_{0.2}\text{LaCuO}_5$	3.827	8.948	0.854	
$\text{TlBa}_{0.6}\text{Ca}_{0.4}\text{LaCuO}_5$	3.817	8.885	0.847	14
$\text{TlBa}_{0.4}\text{Ca}_{0.6}\text{LaCuO}_5$	3.790	8.815	0.841	16
$\text{TlBa}_{0.2}\text{Ca}_{0.8}\text{LaCuO}_5$	3.766	8.750	0.834	13

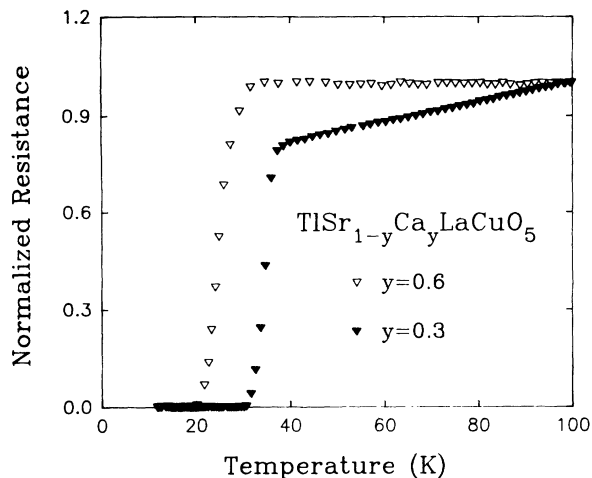


FIG. 3. Normalized resistance as a function of temperature in  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$  ( $x = 0.3, 0.6$ ).

#### IV. DISCUSSION

##### A. Structural stability and role of thallium

Careful analysis of x-ray powder-diffraction patterns revealed the presence of a trace of  $\text{La}_2\text{CuO}_4$  as impurity phase in the materials  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$  and  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$ . The intensity of the impurity lines increases with increasing  $y$  in  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$ . In the system  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  the impurity phase appears with  $z = 0.8$ , as shown in Fig. 2. The stability of the tetragonal 1:2:0:1 phase of these systems could be understood in terms of a geometrical factor, the so-called tolerance factor, as discussed below.

All the known copper oxide superconductors are built up of oxygen-deficient perovskite layers intergrown with

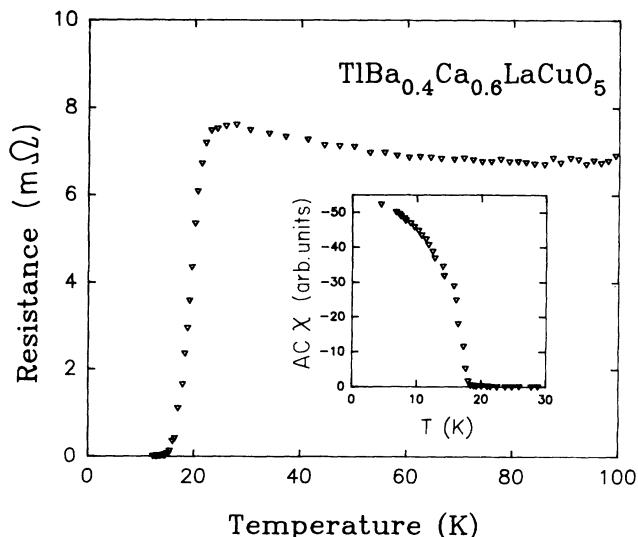


FIG. 4. Resistance as a function of temperature of  $\text{TlBa}_{0.4}\text{Ca}_{0.6}\text{LaCuO}_5$ . The inset shows the diamagnetic response, as a function of temperature; the estimated superconducting volume fraction is in excess of 60%.

rocksalt or fluorite-type layers. In general, perovskite layers are made up of copper and oxygen, and, particularly in thallium compounds, the rocksalt or fluorite-type layers are Tl, Ba or Sr, Ca or rare earths, and oxygen. Stabilization of the intergrowth structure requires bond-length matching across the intergrowth interface. A measure of bond-length matching across the interface is the tolerance factor,<sup>15</sup>  $t = r_{A-O} / \sqrt{2} r_{\text{Cu-O}}$ , where  $A$  represents the ions in the rocksalt or fluorite-type layers and  $r_{A-O}$  is the average length of the  $A$ -O bonds in the structure. An ideal matching occurs when  $t = 1$ .  $t < 1$  means that the  $\text{CuO}_2$  planes are under compression and the  $A$ -O layers are under tension.<sup>16</sup> The empirically observed limits for the stability of the intergrowth structure are  $0.86 \leq t \leq 1.02$ .<sup>17</sup>

The tolerance factor for  $\text{TlBa}_{1-x}\text{Sr}_x\text{LaCuO}_5$  ( $0 \leq x \leq 1$ ),  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$  ( $0 \leq y \leq 0.6$ ), and  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  ( $0 \leq z \leq 0.8$ ) has been calculated according to the above relation using the average radii of the  $A$  ions, taken from Ref. 18, for the appropriate coordination number. Values of  $t$  for various materials are shown in Table I.

The tolerance factor for the semiconducting  $\text{TlBaLaCuO}_5$  is 0.860, which lies right at the lower limit for the stability of the intergrowth structure. Upon substituting Sr at the Ba site, and considering that Tl remains in the 3+ state (so that its effective radius does not vary as a function of doping), the tolerance factor decreases below the lower limit (see Table I), due to the smaller ionic radius of Sr, which means that the structure should not form. The fact that the structure forms (and therefore the tolerance factor must be within the stability limits), and the phase is stabilized, however, suggests that the valence of the Tl ions does change; it moves toward 1+ and the ions expand in size (radius = 0.885 Å for  $\text{Tl}^{3+}$  and 1.50 Å for  $\text{Tl}^{1+}$  for six coordination). These studies, therefore, clearly throw light on the dual role of thallium in these materials, i.e., it stabilizes the structure by varying its size and allows the generation of holes, via the redox mechanism, by changing its valence. Of course, at the same time, the decrease in  $r_{\text{Cu-O}}$  (see below) due to the creation of holes in the  $\text{CuO}_2$  planes also contributes to the increase in the effective value of the tolerance factor.

The solubility of Ca is limited by the tolerance factor  $t = 0.834$ , which is the limiting value for Ca in  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$  and  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$ . Beyond the value of  $t = 0.834$  the impurity phase dominates. Large concentrations of such ions correspond to a large fraction of monovalent Tl, which the lattice finds too difficult to accommodate because of its bigger ionic radius (1.50 Å).

##### B. Overdoping in $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$

The lattice parameters  $a$  and  $c$  decrease with increasing  $y$  (see Table I). Decrease of  $c$  with increase of  $y$  implies that the  $\text{Ca}^{2+}$  ions substitute essentially for  $\text{Sr}^{2+}$  ions. Decrease of lattice parameter  $a$  with increase of  $y$  shows that the in-plane Cu-O bond length  $r_{\text{Cu-O}}$  decreases, which should increase the overlap of the Tl 6s and Cu  $3d_{x^2-y^2}$  bands and thereby increase the hole concentra-

tion. The decrease of  $T_c$  for  $y = 0.6$  reveals that the material is in the overdoped state. The variation of  $T_c$  with hole concentration in the systems  $\text{TlBa}_{1-x}\text{Sr}_x\text{LaCuO}_5$  and  $\text{TlSr}_{1-y}\text{Ca}_y\text{LaCuO}_5$ , as a whole, is similar to what has been observed in the other high- $T_c$  superconductors.

### C. Superconductivity in $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$

In order to check the validity of the creation of the redox mechanism and thus the semiconductor-metal transition in  $\text{TlBaLaCuO}_5$  by substituting smaller alkaline rare earths ( $\text{Sr}^{2+}$ ) at the Ba site and further  $\text{Ca}^{2+}$  at the Sr site in  $\text{TlSrLaCuO}_5$ , we have substituted  $\text{Ca}^{2+}$  at the Ba site in  $\text{TlBaLaCuO}_5$ . Decrease of the lattice parameters  $a$  and  $c$  with increase of  $z$  in  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  suggests that the in-plane Cu-O bond length decreases, which should favor the overlap of Tl 6s and Cu  $3d_{x^2-y^2}$  bands at the Fermi level, and Ca essentially substitutes at the Ba site. The observation of superconductivity in  $\text{TlBa}_{1-z}\text{Ca}_z\text{LaCuO}_5$  for  $0.3 < z < 0.8$  proves the existence or creation of the redox mechanism when the lattice parameter  $a$  is small or made smaller. It is important to note that the compound  $\text{TlCaLaCuO}_5$  does not form, presumably again in accordance with the consideration of the tolerance factor. It is

instructive to note that our attempt to prepare single-phase  $\text{TlBaLaCuO}_5$ , substituted with smaller rare earths at the bigger La site, which is also expected to decrease the in-plane Cu-O bond length and hence favor overlap of Tl 6s and Cu  $3d_{x^2-y^2}$  bands, was not successful. This may be due to the increase of the mismatch between  $\text{Ba}^{2+}$  and the smaller rare earths.

### V. CONCLUSIONS

We have shown here that, using the concept of the *redox mechanism*, the hole concentration can be increased in  $\text{TlSrLaCuO}_5$  by substituting a smaller isovalent cation ( $\text{Ca}^{2+}$ ) at the bigger Sr site, leading to an overdoped region. Based on this model, we have also been able to induce superconductivity in the semiconducting  $\text{TlBaLaCuO}_5$  by substituting a smaller isovalent cation ( $\text{Ca}^{2+}$ ) at the bigger Ba site. Structural-stability considerations give useful information with respect to the solubility limit of the substituent and the valence state of thallium.

### ACKNOWLEDGMENTS

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