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# Structure of the new “1201” lead cuprate superconductor

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The structure of the newly discovered “1201” lead cuprate superconductor  $(\text{Pb, Cu})(\text{Sr, La})_2\text{CuO}_{5-\delta}$  with  $T_c = 27.5$  K at onset and a shielding fraction 38% at 5 K and 10 Oe, has been determined using neutron powder diffraction. The structure is similar to the other 1201 materials  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$  and  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$  (where the former superconductors with a  $T_c$  of 52 K and the latter is not superconducting), belonging to the space group  $\text{P4}/\text{mmm}$ . The doping scheme in  $(\text{Pb, Cu})(\text{Sr, La})_2\text{CuO}_{5-\delta}$  combines the doping scheme used in these two compounds, in that both the Tl and Sr sites are doped. The starting stoichiometry, the refined scale factors for the impurity phases and the refined site occupancies for oxygen suggests that the stoichiometry (relative to Cu) of the superconducting phase is  $\text{Pb}_{0.60}\text{Cu}_{0.40}\text{Sr}_{1.08}\text{La}_{0.92}\text{CuO}_{4.96}$ . Calculation of the average hole concentration in these compounds from charge summation is difficult with these compounds because the Tl/Pb–O layers provide polarizable charge reservoirs that can participate in substantial covalent bonding and because of the probable mixed-valent nature of Tl and Pb. Nevertheless, bond valence sums calculated for the Cu ions in the  $\text{CuO}_2$  layers for the three 1201 cuprates do provide a correlation with the values of  $T_c$  or the absence of superconductivity.

## 1. Introduction

In the homologous series of single-thallium-layer cuprate superconductors [1], represented by  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  ( $n=1$  to 5), it has been possible to replace half the thallium with lead in all the barium with strontium to give compounds of composition  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  [2–4]. The structure essentially consists of Ba (or Sr)–Cu–(Ca)–O oxygen deficient perovskite slabs which are interconnected by a rock-salt like AO layer, where A is Tl or (Tl, Pb). The great range of available cations that can be doped into these compounds offers us the opportunity to study the relationship between crystal structure, hole doping and superconductivity. Superconductivity in these compounds is believed to originate from the presence of holes in the  $\text{CuO}_2$  sheets and the average oxidation state of the  $\text{CuO}_2$  sheets can be controlled by changing the chemistry of these materials. The mechanisms for hole doping include cation substitution [5], cation vacancies [6], insertion of oxygen [7], and internal redox mechanisms of the type  $\text{Tl}^{3+} + 2e \rightarrow \text{Tl}^{1+}$  [8].

We have been studying the structure and super-

conductivity of the first member of this series, with  $n=1$ , generally referred to as the “1201” compounds.  $\text{TlBa}_2\text{CuO}_5$  does not superconduct because it is overdoped with too high a hole concentration in the  $\text{CuO}_2$  sheets. Thus, superconductivity can be induced through the partial substitution of trivalent rare earth ions for  $\text{Ba}^{2+}$  and  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$  is a superconductor with a  $T_c \approx 52$  K [9]. However, partially doping  $\text{TlSr}_2\text{CuO}_5$  in the Tl–O planes with  $\text{Pb}^{4+}$  to what is expected to be nearly the same hole concentration does not produce superconductivity [10]. Presumably, the sort planar Cu–O bond constrains the  $\text{CuO}_2$  sheets to too high a hole concentration despite doping in the Tl/Pb–O planes. Recently, Adachi et al. [11] reported superconductivity with  $T_c$  (zero resistance) at 25 K in a 1201 material with nominal composition  $\text{Pb}_{0.6}\text{SrLaCu}_{1.5}\text{O}_{5-\delta}$ , in which all of the Tl has been replaced by Pb and Cu. Thus the charge reservoir, now presumably consisting of  $\text{Pb}^{4+}/\text{Cu}^{2+}$ –O layer, has approximately the same average oxidation states as the Tl–O layers in  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$ . Doping of  $\text{La}^{3+}$  for  $\text{Sr}^{2+}$ , analogous to the doping in  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$ , should decrease the hole concentration to a value favorable for

superconductivity. However, the reported lattice constant  $a=3.78 \text{ \AA}$  [11] implies a short in-plane Cu–O bond length of  $1.89 \text{ \AA}$ , only slightly larger than the  $1.87 \text{ \AA}$  for the Cu–O bond in  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$ . Thus  $(\text{Pb}, \text{Cu})(\text{Sr}, \text{La})_2\text{CuO}_{5-\delta}$  is interesting because it shares some similarities with  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$  that are favorable for superconductivity, while sharing others with  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$  that are not.

This article reports the synthesis and structural characterization, using neutron powder diffraction, of  $(\text{Pb}, \text{Cu})(\text{Sr}, \text{La})_2\text{CuO}_{5-\delta}$  in order to better understand its structure, particularly the Cu–O bonds lengths, the cation ratios in the mixed cation Pb/Cu and Sr/La sites, and the oxygen stoichiometry. These results allow us to correlate the structure and estimated hole concentration with superconductivity.

## 2. Experimental procedure and data analysis

A 25 g sample was prepared from starting powders  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{CuO}$ , so as to give the metal composition  $\text{Pb}_{0.6}\text{SrLaCu}_{1.5}\text{O}_{5-\delta}$ , using the procedure outlined by Adachi et al. As shown in fig. 1, resistance measurements indicated that the sample is superconducting with a  $T_c$  (onset) of 27.5 K and a  $T_c$  (zero resistance) of 23.5 K. The broadening of the lower half of the transition and lower  $T_c$  (zero)

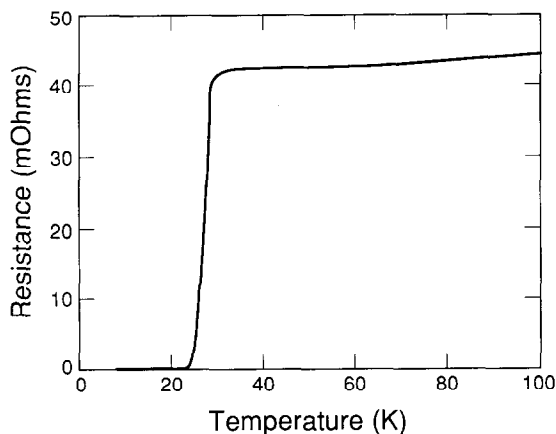


Fig. 1. Resistance of  $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{SrLaCuO}_{5-\delta}$  as a function of sample temperature.

probably arises from imperfections at the grain boundaries [12]. Susceptibility measurements, the results of which are shown in fig. 2, also gave a  $T_c$  (onset) of 27.5 K, a shielding fraction of 38% and a Meissner fraction of 16%, the latter two at 6 K.

Neutron-powder-diffraction data were collected at 300 K on the high intensity powder diffractometer (HIPD) at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) at the Los Alamos National Laboratory. Data were collected in four detector banks (at approximately  $\pm 153^\circ$  and  $\pm 90^\circ$ ) for approximately 1 h at an average proton current of approximately  $80 \mu\text{A}$ . The structural models were refined using the Rietveld refinement code developed by Larson and Von Dreele [13]. The data taken was indexed with the tetragonal space group  $\text{P4/mmm}$ . The structural parameters refined for  $(\text{Pb}, \text{Cu})(\text{Sr}, \text{La})_2\text{CuO}_{5-\delta}$  include the lattice constants, atomic positions, anisotropic thermal parameters, and site occupancy. As in the structures for other 1201 compounds, atoms in the Pb/Cu–O3 plane displayed large in-plane thermal parameters, and displacements in the [100] and the [110] directions were used to model the disordering of Pb/Cu and O3 in the  $a$ – $b$  plane. O3 displacements of the type  $(x, 1/2, 0)$  gave values of weighted profile agreement factors,  $R_{\text{wp}}$ , that were considerably lower (by 0.33–0.35%) than displacements of the type  $(x, x, 0)$ . For Pb/Cu,  $R_{\text{wp}}$  for the various displacement models dif-

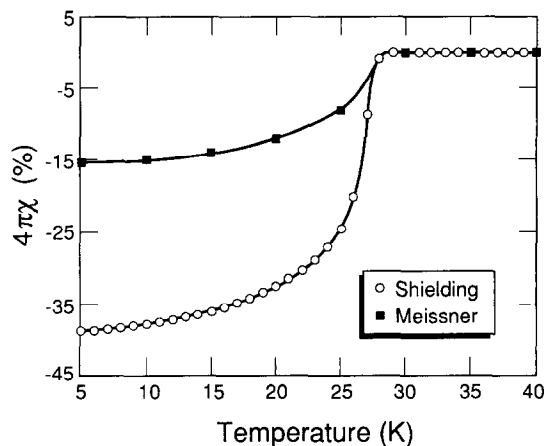


Fig. 2. Dependence of the magnetic susceptibility on sample temperature. Measurements were performed in an applied field of 10 Oe and demagnetization effects were accounted for in calculating the percent diamagnetism.

ferred less, this time with the  $(x, 0, 0)$  positions favored over the  $(x, x, 0)$  positions by 0.02–0.04%. As a consequence, the displacement sites  $(x, 0, 0)$  and  $(x, 1/2, 0)$ , with isotropic thermal parameters, were used to model the atomic positions for Pb/Cu and O3, respectively. In addition to the structural parameters shown in table 1, background, scale factor, absorption, extinction and anisotropic strain were also fitted.

The nonstoichiometric starting composition suggests that impurities would be present. In fact, we found that PbO, CuO and La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> were all present in addition to the parent (Pb, Cu)(Sr, La)<sub>2</sub>CuO<sub>5-δ</sub>; these were included as second, third and fourth phases in the refinement. Since these impurity phases were only present at relatively low levels (at 1.2, 2.0, and 5.8 wt.% for PbO, CuO and

La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>, respectively, we fixed the isotropic thermal parameters for the cations and oxygen ions at 0.010 and 0.015 Å and refined only the scale factors, lattice constants and atomic positions for these three phases.

The initial stoichiometry and the refined phase fractions of these impurities suggested that the Pb/Cu and Sr/La ratios for the two mixed cation sites in (Pb, Cu)(Sr, La)<sub>2</sub>CuO<sub>5-δ</sub> must be 1.50 and 1.17, respectively, which are to be compared with the expected ratios of 1.5 and 1.0, respectively. These values were then used without further refinement for the relative site occupancies for Pb/Cu and Sr/La in the refinement of the structure for Pb<sub>0.60</sub>Cu<sub>0.40</sub>Sr<sub>1.08</sub>La<sub>0.92</sub>CuO<sub>5-δ</sub>.

During the initial refinements for oxygen site occupancy, the O1 site occupancy would refine to values slightly greater than unity and was consequently set 1.0 and not further refined. The site occupancies for O2 and O3 refined to a values of 0.970(4) and 0.249(4), respectively. If we take into account the multiplicity of 2 for the O1 and O2 sites and 4 for the displaced O3 site, this then gives a value of  $\delta = 0.04$ .

Portions of the data collected with the +153° detector bank and the fits from the structural refinement are shown in fig. 3. The results for the struc-

Table 1

Structural parameters for Pb<sub>0.60</sub>Cu<sub>0.40</sub>Sr<sub>1.08</sub>La<sub>0.92</sub>CuO<sub>5-δ</sub> at 300 K. Space group P4/mmm: Pb/Cu( $x, 0, 0$ ), Sr/La( $1/2, 1/2, z$ ), Cu( $0, 0, 1/2$ ), O1( $0, 0, z$ ), O2( $1/2, 0, 1/2$ ) and O3( $x, 1/2, 0$ ). Units for thermal parameters are  $10^{-2}$  Å<sup>2</sup>. The numbers in parentheses following refined parameters represent the estimated standard deviations in the last significant digit.

Parameter	Refined value
$a$ (Å)	3.78607(4)
$c$ (Å)	8.65615(18)
Pb/Cu	$f$ 0.6/0.4
	$x$ 0.0701(6)
Sr/La	$U_{iso}$ 1.41(6)
	$f$ 0.54/0.46
	$z$ 0.28814(10)
	$U_{11} = U_{22}$ 1.43(3)
	$U_{33}$ 1.01(5)
Cu	$U_{11} = U_{22}$ 0.39(3)
	$U_{33}$ 1.51(6)
O1	$f$ 1
	$z$ 0.22279(18)
	$U_{11} = U_{22}$ 3.90(6)
	$U_{33}$ 4.19(11)
O2	$f$ 0.970(4)
	$U_{11}$ 0.08(4)
	$U_{22}$ 0.79(5)
	$U_{33}$ 4.05(11)
O3	$f$ 0.249(4)
	$x$ 0.3330(8)
	$U_{iso}$ 3.13(14)
$d$ spacing range (Å)	0.4–6.65
$R_{wp}/R_{exp}$ (%)	4.68/3.05

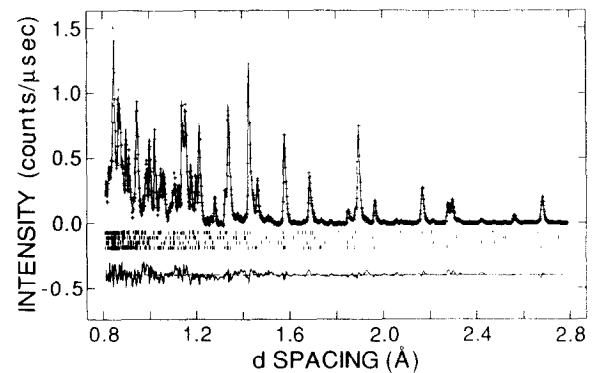


Fig. 3 Part of the neutron-diffraction data for (Pb,Cu)(Sr, La)<sub>2</sub>CuO<sub>5-δ</sub>. Data shown by plus (+) symbols are data taken on the +153° detector band of the HIPD at a sample temperature of 300 K. The continuous lines through the sets of points are the calculated profiles from Rietveld refinement. The sets of ticks below the data indicate the positions for the allowed reflections for (Pb,Cu)SrLaCuO<sub>5-δ</sub>, PbO, CuO and La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> in ascending order. The lower curve represents the difference between observed and calculated profiles.

tural refinements are given in table 1 and an ORTEP plot [14] of the structure is shown in fig. 4.

### 3. Results and discussion

The refined lattice constants [ $a=3.78608(4)$  and  $c=8.65623(18)$  Å] differ from those for the undoped parent compound  $\text{TlSr}_2\text{CuO}_5$  [ $a=3.7344(5)$  and  $c=9.007(1)$  Å] in that  $a$  is longer and  $c$  is shorter. Thus the substitution of the smaller  $\text{La}^{+3}$  for  $\text{Sr}^{+2}$  and the smaller  $\text{Pb}^{+4}/\text{Cu}^{+2}$  for  $\text{Tl}^{+3}$  leads to an expected decrease in  $c$  but a surprising increase in  $a$ . Comparison of the lattice constants with those for superconducting  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$  [ $a=3.8479(3)$  and  $c=9.0909(6)$  Å] and nonsuperconducting  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$  [ $a=3.7309(3)$  and  $c=8.9983(8)$  Å] show that  $c$  is shorter than either but that  $a$  lies in between. Table 2 provides a comparison of selected bond lengths for  $\text{Pb}_{0.6}\text{Cu}_{0.4}\text{SrLaCuO}_5$  with those for  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$  and  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$ . Since the average ionic radius of  $\text{Sr}^{+2}/\text{La}^{+3}$  is smaller than that for  $\text{Ba}^{+2}/\text{La}^{+3}$  or for  $\text{Sr}^{+2}$  alone, the main effect of partially doping  $\text{La}^{+3}$  for  $\text{Sr}^{+2}$  would be expected to reduce both  $a$  and  $c$ . However, while the  $\text{Sr}/\text{La}-\text{O}3$  distance is substantially shorter as ex-

pected, distances to the other oxygens are actually slightly longer. The ionic radii for  $\text{Pb}^{+4}$  and  $\text{Cu}^{+2}$  are both very small, resulting in short axial  $\text{Pb}/\text{Cu}-\text{O}1$  bonds and displacements in the  $\text{Pb}/\text{Cu}-\text{O}3$  layer are much larger than corresponding displacements for  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$  or  $\text{TlBa}_{1.2}\text{La}_{0.8}\text{CuO}_5$ . Thus both the  $\text{Sr}/\text{La}-\text{O}1$  and the  $\text{Pb}/\text{Cu}-\text{O}3$  layers are under considerable tensile strain. The shorter  $\text{Sr}/\text{La}-\text{O}$  distances and the small size of  $\text{Pb}/\text{Cu}$  must exert a significant compressive strain on the  $\text{CuO}_2$  layer along both  $a$  and  $c$  axes, with the resultant small axial  $\text{Cu}-\text{O}1$  and intermediate in-plane  $\text{Cu}-\text{O}2$  bond lengths (see below). These strains may be partially relieved by a transfer of charge from the  $\text{Sr}/\text{La}-\text{O}$  and  $\text{Pb}/\text{Cu}-\text{O}3$  layers to the  $\text{Cu}-\text{O}2$  layer; since  $\text{Pb}^{+2}$  is much larger, some of the strain in that layer may also be relieved if  $\text{Pb}$  becomes mixed-valent. However, no structural transitions from the tetragonal "1201" structures, beyond the larger displacements in the  $\text{Pb}/\text{Cu}-\text{O}3$  layers, take place to relieve the strain.

The dependence of  $T_c$  with  $x$  for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  has been shown to have a dome shaped behavior with a maximum  $T_c$  corresponding to a hole concentration of about 0.18 per  $\text{Cu}-\text{O}$  [15]. Similar studies of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$  [16] and  $\text{Tl}_{2-x}\text{Cd}_x\text{Ba}_2\text{CuO}_{6+\delta}$  [5] have shown that maxima in  $T_c$  correspond to approximately 0.50 holes (assuming the holes are doped into the  $\text{CuO}_2$  sheets) and  $0.3 \pm 0.1$  holes per  $\text{Cu}-\text{O}$ , respectively. Adachi et al.'s study [11] of  $\text{Pb}_{1-x}\text{Cu}_x\text{SrLaCuO}_5$  and our study [10] of  $\text{TlBa}_{2-x}\text{La}_x\text{CuO}_5$  have shown that these compounds have maxima in  $T_c$  at compositions with  $x=0.4$  and  $0.8$ , respectively, while our study [9] of  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$  has shown that it is not superconducting. If we assume that  $\text{Tl}$  and  $\text{Pb}$  have oxidation states  $+3$  and  $+4$ , and  $\text{Cu}$  in the  $\text{Pb}/\text{Cu}$  layer an oxidation state  $+2$ , then the doping levels calculated from charge summation are  $-0.20$ ,  $+0.40$  and  $+0.53$  per  $\text{Cu}-\text{O}$ , respectively, for the three compounds. The negative hole concentration for  $\text{Pb}_{1-x}\text{Cu}_x\text{SrLaCuO}_5$  obtained this way cannot be correct for a hole doped superconductor and suggests that  $\text{Pb}$  must be mixed-valent. For example, if  $\text{Pb}$  has an oxidation state of  $+2$  instead, then the hole concentration in the  $\text{CuO}_2$  sheets in  $\text{Pb}_{0.6}\text{Cu}_{0.4}\text{SrLaCuO}_5$  is  $+1.0$ ; thus, mixed valency could easily result in a more optimum value of the hole concentration. This is consistent with a more

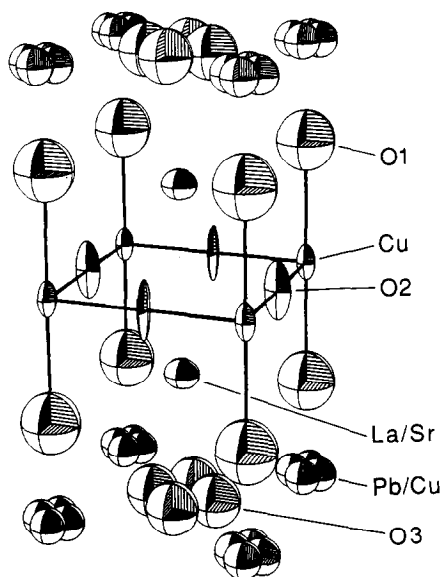


Fig. 4. The structure of  $(\text{Pb}, \text{Cu})(\text{Sr}, \text{La})_2\text{CuO}_{5-\delta}$  at 300 K. The thermal ellipsoids are drawn as 95% probability surfaces.

Table 2

Comparison of lattice constants and selected interatomic distances (Å) for Pb<sub>0.6</sub>Cu<sub>0.4</sub>SrLaCuO<sub>5</sub> at 300 K, with TlBa<sub>1.2</sub>La<sub>0.8</sub>CuO<sub>5</sub> at 305 K [9] and Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>CuO<sub>5</sub> at 300 K [10]. The numbers in parentheses following the bond distances represent the estimated standard deviations in the last significant digit(s).

Distance	Pb <sub>0.6</sub> Cu <sub>0.4</sub> SrLaCuO <sub>5</sub>	Tl <sub>0.5</sub> Pb <sub>0.5</sub> Sr <sub>2</sub> CuO <sub>5</sub>	TlBa <sub>1.2</sub> La <sub>0.8</sub> CuO <sub>5</sub>
Cu–O1	2.3996(16)	2.4914(7)	2.500(1)
Cu–O2	1.89304(2)	1.8654(15)	1.9240(1)
Sr–O1	2.7363(4)	2.7177(3)	2.7924(2)
Sr–O2	2.6356(6)	2.6192(4)	2.6840(2)
Sr–O3	2.5731(11)	2.6837(6)	2.6883(2)
Tl/Pb–O1	1.9466(16)	2.0217(7)	2.069(1)
Tl/Pb–O3	2.1389(16)–3.0043(29)	2.2236(19)–2.7509(18)	2.307(2)–2.774(2)

recent study, where a titrimetric technique was applied to the double thallium layer cuprates Tl<sub>2</sub>Ba<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4</sub> ( $n=1$  and  $2$ ) to determine both the Tl and the oxygen contents [18]; these studies suggested that Tl must be mixed-valent if the formal oxidation state of Cu is greater than 2, as would be expected for a hole superconductor. If Tl is indeed mixed valent, then the hole concentrations for Tl<sub>2-x</sub>Cd<sub>x</sub>Ba<sub>2</sub>CuO<sub>6+δ</sub> and TlBa<sub>1.2</sub>La<sub>0.8</sub>CuO<sub>5</sub> calculated from charge summation may be too small, and likewise for Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>CuO<sub>5</sub> if both Tl and Pb, or either, are mixed valent.

The oxidation state of the Pb ions in these kinds of compounds have been estimated from X-ray absorption near-edge spectroscopy (XANES) and from the Pb–O3 bond lengths, but neither method is quantitative. An earlier structural study of Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+3</sub> ( $n=2$  and  $3$ ) made use of separate XANES measurements to determine the oxidation state of Pb [17]. A comparison of the near-edge features at the Pb L<sub>III</sub> edge for both superconductors with those for PbO and PbO<sub>2</sub> showed a strong similarity to the latter and suggested that the valence of Pb in the superconductors is predominantly +4. A similar study showed that the XANES spectrum for Tl in Tl<sub>2-x</sub>Cd<sub>x</sub>Ba<sub>2</sub>CuO<sub>6+δ</sub> showed the pre-edge features characteristic of Tl<sup>+3</sup>; however, it was felt that this result does not rule out the existence of Tl<sup>+1</sup>/Tl<sup>+3</sup> mixed valence but instead shows that the average oxidation state of Tl does not change with Cd substitution [5]. Sums of ionic radii [19] give an expected bond length of 2.59 Å for symmetric octahedrally coordinated Pb<sup>+2</sup>–O<sup>-2</sup> and 2.175 Å for similarly coordinated Pb<sup>+4</sup>–O<sup>-2</sup>. Cu<sup>+2</sup> tends to form

distorted octahedral complexes with oxygen, with four short bonds (about 1.93 Å) and two long axial bonds (about 2.25 Å). The lattice parameter  $a$  constrains the average length of the in-plane Pb/Cu–O3 bond to 2.677 Å, while the length of the axial Pb/Cu–O1 bonds is 1.94 Å. This results in four long and two short bonds for the Pb/Cu–O1, O3 octahedra that differ substantially from the expected geometry for symmetric PbO<sub>6</sub> octahedra or distorted CuO<sub>6</sub> octahedra. This frustration of the optimum bonding and coordination for the oxygens is relieved by displacements of the constituents in Pb/Cu–O3 planes to give four short Pb/Cu–O bonds (two in-plane and two axial) and two long Pb/Cu–O bonds. In fact, the displacements of both Pb/Cu and O3 from their ideal sites result in two short bonds at approximately 2.22 Å and two long bonds at approximately 2.75 Å in the Pb/Cu–O3 plane. Thus neither the EXAFS results nor the lengths of the Pb/Cu–O bonds sheds much light on the oxidation states of the Pb ions.

Since the mixed-valent nature of the Pb/Cu–O3 layer makes it difficult to determine the hole concentration in the Cu–O layers from charge summation, we instead try to estimate the hole doping from valence bond sums for the CuO<sub>2</sub> sheets [20,21]. Following the work of Brown [21], we can calculate Cu bond valence sums

$$V = \sum s_i = \sum \exp[(R_0 - R_i)/\beta]$$

for the CuO<sub>2</sub> sheets using values for the parameters  $R_0$  and  $\beta$  provided by Brown [21] and Brown and Altermatt [22]. Use of the parameters for Cu<sup>+2</sup> gives values of +2.280, +2.528 and +2.668 for the valence sums for Cu in Tl<sub>1.2</sub>La<sub>0.8</sub>CuO<sub>5</sub>,

Pb<sub>0.5</sub>Cu<sub>0.5</sub>LaSrCuO<sub>5</sub> and Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>CuO<sub>5</sub>, respectively. If instead, valence sums for Cu<sup>+3</sup> are also calculated and the proportion  $y$  of Cu<sup>+3</sup> is determined from the equation [21],

$$y = (V_2 - 2) / (V_2 + 1 - V_3),$$

where  $V_2$  and  $V_3$  are the valence sums for Cu calculated from the values of  $R_0$  for Cu<sup>+2</sup> and Cu<sup>+3</sup> (1.679 and 1.730 Å, respectively) given by Brown [21], then more correctly calculated valence sums for Cu of +2.618, +2.902 and +3.058, respectively, are obtained. The valence sums calculated either way undoubtedly give values of the valence sums for the 1201 cuprates that are too high because of the existence of structural constraints, but the qualitative trends are undoubtedly correct. The in-plane Cu–O<sub>2</sub> bond distances in these compounds are all constrained to too small a value by constraints in the crystal structure when compared with the ideal bond lengths predicted by the valence sum rule. Thus the CuO<sub>2</sub> layers are in states of increasing compression as the Cu–O<sub>2</sub> bond lengths decrease. Unfortunately, the uncertainty in the actual bond lengths in the Pb/Cu–O<sub>3</sub> layer and the great disparity in actual and expected geometries makes similar estimates of the oxidation states for Pb and Cu from bond valence sums difficult.

Recently, de Leeuw et al. [23] noted that most high  $T_c$  superconductors have maximum values of  $T_c$  when the holes per Cu atom is about +0.2. However, they observed a correlation between these maximum  $T_c$ s and Cu valences calculated from bond valence sums, which varied from +2.06 to +2.53. Noting that bond valence sums for both the Cu and the equatorial oxygens decreased with increasing  $T_c$ , they further suggested that the higher transition temperatures involve a progressive transfer of holes from the oxygens to the Cu. This latter conclusion is disputed by Brown [24], who correctly points out that the distribution of holes cannot be deduced from bond valence sums. Instead, Brown attributes deviations in the bond valence sums to internal strain, with the higher transition temperatures stabilized when the CuO<sub>2</sub> layers are in tension. Nevertheless, the correlation between  $T_c$  and Cu bond valence sums (using parameters for Cu<sup>+2</sup>) observed by de Leeuw et al. is quite intriguing. Since Pb<sub>0.6</sub>Cu<sub>0.4</sub>LaSrCuO<sub>5</sub> and TlBa<sub>1.2</sub>La<sub>0.8</sub>CuO<sub>5</sub> are both doped to give the maxi-

imum value for  $T_c$  for that series, with  $T_c$ 's (onset) of 27.5 and 52 K, respectively, it is interesting to note that the bond valence sums (+2.280 and +2.528, respectively) calculated using the same parameters follow the trend noted by de Leeuw et al. as shown in fig. 5. The valence sum for the Cu ions in Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>CuO<sub>5</sub> of +2.668 is too large to support superconductivity.

Since all of the 1201 cuprates have polarizable and probably mixed-valent Pb/Cu–O, Tl–O or Tl/Pb–O layers, the calculation of hole concentrations based on summation of oxidation states is difficult. This is a reflection of the possible covalent bonding and the more complicated redox chemistry that is available with the Tl/Pb–O layers in these systems. The length of the Cu–O bonds may provide an alternate measure of the hole concentration in the Cu–O planes, although internal strain in these crystals result in overestimates of the Cu valence. We find that the Cu–O in-plane distance, which provides the dominant contribution to the valence sum, in Pb<sub>0.6</sub>Cu<sub>0.4</sub>LaSrCuO<sub>5</sub> is 1.893 Å, shorter than the equivalent bond in TlBa<sub>1.2</sub>La<sub>0.8</sub>CuO<sub>5</sub> (at 1.915 Å) and longer than the Cu–O bond in Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>CuO<sub>5</sub> (at 1.865 Å). The resulting valence sums for Cu in

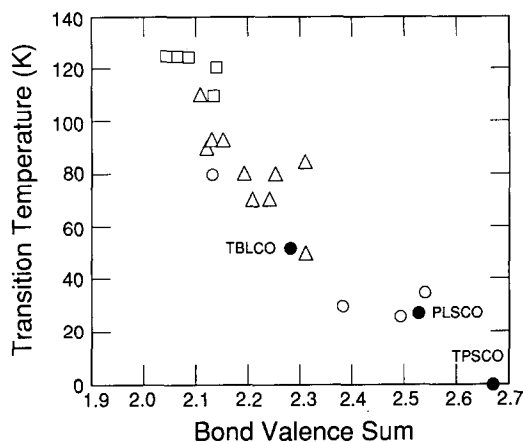


Fig. 5. Maximum values of the critical temperature as a function of bond valence sums calculated using values of the parameters ( $R_0 = 1.679$  Å and  $\beta = 0.37$  Å) corresponding Cu<sup>+2</sup>–O<sup>2-</sup> (adapted from ref. [23]). Data points from ref. [23] are indicated by open figures (with 4, 5 and 6 oxygens coordinating each copper denoted by open squares, triangles and circles, respectively). The three filled circles are for TlBa<sub>1.2</sub>La<sub>0.8</sub>CuO<sub>5</sub> (denoted TBLCO), Pb<sub>0.6</sub>Cu<sub>0.4</sub>LaSrCuO<sub>5</sub> (PLSCO), and Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>CuO<sub>5</sub> (TPSCO).

TlBa<sub>1.2</sub>La<sub>0.8</sub>CuO<sub>5</sub>, Pb<sub>0.5</sub>Cu<sub>0.5</sub>LaSrCuO<sub>5</sub> and Tl<sub>0.5</sub>Pb<sub>0.5</sub>Sr<sub>2</sub>CuO<sub>5</sub> correlate well with the  $T_c$ s of 52 and 27.5 K for the first two compounds, which are superconductors, and with the absence of superconductivity in the third compound. Thus the hole concentration in the Cu–O sheets, calculated from the length of the in-plane and axial Cu–O bonds, provide a useful correlation with superconductivity as noted earlier by de Leeuw et al. [23].

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