

# Stabilization of Thallium Strontium “1212” and “2212” Superconducting Cuprates by Mercury

A. Maignan, C. Martin, C. Michel, M. Hervieu,\* and B. Raveau

Laboratoire CRISMAT, CNRS URA 1318, ISMRA et Université de Caen,  
Bd du Maréchal Juin 14050 CAEN Cédex, France

Received December 13, 1994. Revised Manuscript Received March 22, 1995<sup>®</sup>

The exploration of the system Tl–Hg–Sr–Ca–Cu–O has allowed a 2212 superconducting thallium strontium based cuprate,  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ , to be isolated for the first time, with a  $T_c$  of 25 K. In the same way, the 1212 superconducting cuprate,  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$ , with a  $T_c$  of 65 K has been prepared as a nearly pure phase. The combined XRD, ED, HREM, and EDS studies of these phases show the presence of an excess of strontium in the calcium sites and allows a cationic distribution to be proposed. Moreover, for intermediate compositions, one observes complex intergrowths, with  $T_c$ 's ranging from 30 to 60 K.

## Introduction

A huge family of superconducting thallium cuprates has been discovered in the past seven years, with critical temperatures ranging up to 130 K. Most of these compounds belong to the Tl–Ba–Ca–Cu–O system (TBCC) and are now well characterized as well from the structural as from the physical view point (see for review refs 1–3). Unlike the barium cuprates, the number of superconductors that have been isolated in the system Tl–Sr–Ca–Cu–O system (TSCC) is very limited. Superconductivity in the TSCC system, between 40 and 100 K, was detected successively by Sheng et al.,<sup>4</sup> Nagashima et al.,<sup>5</sup> Matsuda et al.,<sup>6</sup> Hayri and Greenblatt,<sup>7</sup> and Martin et al.<sup>8</sup> Unfortunately, all the samples that have been prepared in the TSCC system are multiphase, so that it is difficult to identify the phases which are responsible for superconductivity. Nevertheless, the existence of the “1212” superconducting cuprate  $\text{TlSr}_2\text{CaCu}_2\text{O}_{7-\delta}$ , with  $T_c$ 's ranging from 50 to 70 K, is not questionable.<sup>6,8</sup> Another interesting feature deals with the evidence for superconductivity at 44 K in a multiphase sample of nominal composition  $\text{Tl}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ .<sup>7</sup> The indexation carried out by the authors suggests that the major phase could be a Tl bilayer “2212” cuprate, although a subsequent analysis of their XRD patterns shows that “1212” cuprate is present together with the recently synthesized oxycar-

bonate  $\text{Sr}_4\text{Tl}_2\text{O}_6\text{CO}_3$ .<sup>9</sup> Thus, the existence of the 2212 thallium strontium cuprate, if probable, has not been proved up to date.

A promising route to stabilize the “Tl–Sr” cuprates is to replace partially thallium by a cation with a similar electronic configuration. In this respect Pb(IV) has been proved to be effective, since the nonsuperconducting cuprate  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CuO}_5$ <sup>10</sup> and the 1212 superconductor  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_7$ <sup>11</sup> could be synthesized. In the same way Hg(II), that exhibits a similar  $5d^{10}$  electronic configuration, is a very promising candidate whose possible substitution on the thallium sites has been demonstrated for “Tl–Ba” superconducting cuprates.<sup>12</sup> We report here on two new superconductors, the 1212 cuprate  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$  and the 2212 cuprate  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ , which exhibit critical temperature of 65 and 25 K, respectively.

## Experimental Section

Samples of the Tl–Hg–Sr–Ca–Cu–O system have been prepared starting from mixtures of the oxides  $\text{Tl}_2\text{O}_3$ , HgO, CaO, CuO, and mixtures of  $\text{SrCuO}_2$ , CuO, and  $\text{SrO}_2$ , in order to vary the nominal oxygen content. The pellets are sealed in evacuated silica ampules. After different attempts, the following thermal process has been adopted: the temperature is increased to 800 °C in 10 h, maintained for 30 h, and decreased to 400 °C in 10 h. As it will be detailed in the next section, the syntheses have been carried out in two steps. First, the Tl–Hg–Sr–Ca–Cu–O system was investigated, scanning the compositions  $\text{Tl}_{2-x}\text{Hg}_x\text{Sr}_2\text{CaCu}_2\text{O}_{8-x/2+y}$  (for the 2212's) and  $\text{Tl}_{1-x}\text{Hg}_x\text{Sr}_2\text{CaCu}_2\text{O}_{6.5-x/2+y}$  (for the 1212's); the oxygen content (nominally  $\text{O}_{8-x/2+y}$  and  $\text{O}_{6.5-x/2+y}$ ) was varied, for every nominal  $x$  value. The actual cation compositions ( $x$  value) of the phases were determined by energy-dispersive spectrometry (EDS) on more than 30 crystallites/sample. In a second step, new syntheses have been carried out, following the same process, with nominal  $x$  compositions corresponding to those determined by EDS.

The powder X-ray diffraction (XRD) patterns have been registered by step scanning over an angular range of  $10^\circ \leq$

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, May 1, 1995.

(1) Greenblatt, M.; Li, S.; McMills, L. E. H.; Ramanujachary, K. V. *Studies of high temperature superconductors*; Narlikar, A. V., Ed.; Nova Science Publishers: Commack, NY, 1990, Vol. 15, p 143.

(2) Raveau, B.; Michel, C.; Hervieu, M.; Groult, D. *Crystal Chemistry of High Tc Superconducting Copper Oxides*; Springer Series in Materials Science, No. 15; Springer-Verlag: Berlin, 1991.

(3) *Thallium Based High Temperature Superconductors*; Hermann, A. M.; Yakhmi, J. V., Eds.; Marcel Dekker Press: New York, 1994.

(4) Sheng, Z. Z.; Hermann, A. M.; Vier, D. C.; Schultz, S.; Oseroff, S. B.; George, D. J.; Hazen, R. M. *Phys. Rev. B* **1988**, *36*, 7074.

(5) Nagashima, T.; Watanabe, K.; Saito, H. *Jpn. J. Appl. Phys.* **1988**, *27*, 1077.

(6) Matsuda, S.; Takeuchi, S.; Soeta, A.; Suzuki, T.; Aihara, K.; Kamo, J. *Jpn. J. Appl. Phys.* **1988**, *27*, 2062.

(7) Hayri, E. A.; Greenblatt, M. *Physica C* **1988**, *156*, 775.

(8) Martin, C.; Provost, J.; Bourgault, D.; Doméngès, B.; Michel, C.; Hervieu, M.; Raveau, B. *Physica C* **1989**, *157*, 460.

(9) Caignaert, V.; Hervieu, M.; Goutenoire, F.; Raveau, B. *J. Solid State Chem.*, submitted for publication.

(10) Kwei, G. H.; Shi, J. B.; Ku, H. C. *Physica C* **1991**, *174*, 180.

(11) Subramanian, M. A.; Torardi, C. C.; Gopalakrishnan, J.; Gai, P. L.; Calabrese, J. C.; Askew, T. R.; Flippen, R. B.; Sleight, A. W. *Science* **1988**, *242*, 249.

(12) Goutenoire, F.; Maignan, A.; Van Tendeloo, G.; Martin, C.; Michel, C.; Hervieu, M.; Raveau, B. *Solid State Commun.* **1994**, *90*, 47.

$2\theta \leq 95^\circ$  with an increment of  $0.02^\circ$ , by means of a Philips diffractometer equipped with a secondary graphite monochromator. The cell parameters and structures have been refined using the profile refinement computer program FULLPROF.<sup>13</sup> The electron diffraction (ED) study has been carried out with a JEOL 200CX microscope fitted with an eucentric goniometer and high-resolution electron microscopy (HREM) with a TOPCON 002B microscope, having a point resolution of 1.8 Å. Both microscopes are equipped with a KEVEX analyzer (EDS).

The superconducting properties (zero field cooling) were studied using a SQUID magnetometer with an applied field of 10 G. No demagnetization corrections were made.

## Results

The two series "Tl-Sr" 2212 and 1212 series have been synthesized starting from the nominal compositions  $\text{Tl}_{2-x}\text{Hg}_x\text{Sr}_2\text{CaCu}_2\text{O}_{8-x/2+y}$  (for the 2212's) and  $\text{Tl}_{1-x}\text{Hg}_x\text{Sr}_2\text{CaCu}_2\text{O}_{6.5-x/2+y}$  (for the 1212's) with  $x$  ranging from  $x = 0$  to  $x = 1$  (by steps  $\Delta x = 0.1$ ) and  $y$  ranging from  $y = 0$  to  $y = 2$  (by steps  $\Delta y = 0.4$ ). These as-synthesized samples have been then characterized by XRD, ED, and EDS. Average cation ratios have been determined by EDS, selecting only grains which have been characterized by electron diffraction analysis. At this step, it was observed that, even for samples which appear rather clean from the XRD point of view, the ED investigations and EDS analyses showed that the 2212 and 1212 crystals exhibit actual  $x$  compositions different from the nominal ones. The following observations have been made:

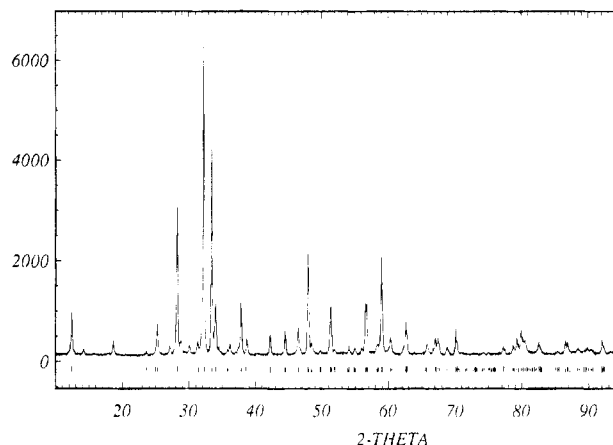
(i) In the two cuprates, 1212's and 2212's, the maximum mercury content is 0.2 per "thallium" layer, i.e.,  $x = 0.2$  for the 1212's and  $x = 0.4$  for the 2212's.

(ii) The actual calcium content is lower than the nominal one, which is one per 1212 unit and the strontium content is, concomitantly, higher than the theoretical one (2.2 Sr per unit instead of 2).

(iii) The ED study shows that there exist secondary phases which are mainly  $\text{Sr}_4\text{Tl}_2\text{O}_6\text{CO}_3$ ,  $\text{CaHgO}_2$ , and defective phases corresponding to disordered intergrowths of the 2212's and 1212's, whose ED patterns are characterized by extra reflections or streaks along the  $c^*$  axis; they are detailed in the HREM section. Note that these defective 2212's and 1212's members are scarcely visible on the XRD patterns so that, even if the XRD patterns of these samples are often rather clean, their magnetic curves exhibit broad transitions.

Coupling systematically EDS and ED analyses, it appears that the crystallites can be classified into three types of material: the "pure" 2212's, the "pure" 1212's, for which sharp reflections are observed in the ED patterns, and the intergrowths of the two members, whose ED patterns are characterized by the superposition of two systems and/or diffuse streaks along  $c^*$ . The average Tl/Hg/Sr/Ca/Cu ratios are 1.5/0.4/2.2/0.8/2 and 0.8/0.2/2.2/0.7/2 for the 2212 and 1212 cuprates, respectively, whereas intermediate compositions are observed for the third class of material, characterized especially by a  $(\text{Tl} + \text{Hg})/\text{Cu}$  ranging from 0.5 to 0.8.

On the bases of these observations, new samples with nominal compositions corresponding to the average ones



**Figure 1.** Powder X-ray diffraction pattern of  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ . The marks correspond to the Bragg angle positions of the "2212" structure.

determined by EDS, have been prepared according to the same thermal treatment; here again, nominal oxygen content was varied, balancing the  $\text{SrCuO}_2/\text{SrO}_2$  ratio, as mentioned above, for the first series of samples.

The nominal compositions were " $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{7.85+y}$ " with  $y = 0, 1, 2$  for the 2212's, " $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{8.5}$ " for the 1212's, and " $(\text{Tl}_{0.8}\text{Hg}_{0.2})_{2-z}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-1.4z}$ " with  $z$  ranging from 0.5 to 0.9 by step of 0.1 for the intergrowths.

**The 2212 Cuprate  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ .** For the nominal composition " $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2$ ", which corresponds to the average cationic content experimentally observed for the 2212 grains, a new phase is obtained which exhibits a XRD pattern characteristic of the 2212 cuprate (Figure 1);  $\text{Sr}_4\text{Tl}_2\text{O}_6\text{CO}_3$  and  $\text{CaHgO}_2$  are still observed but in very small amounts; similar XRD patterns have been observed for  $y$  ranging from 0 to 2. The ED investigation of numerous crystals of the sample confirms that the cell parameters ( $a = b \approx a_p$  and  $c \approx 28.5$  Å) and symmetry (I-type) are those of a 2212 cuprate. No streaks are observed along the  $c^*$  axis as shown from the sharp reflections of the [010] ED pattern (insert in Figure 2).

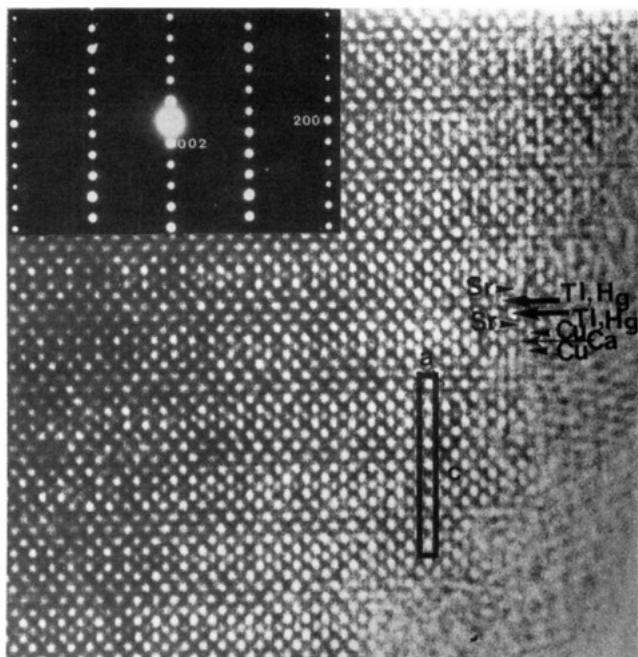
The EDS analysis of more than 50 grains confirms that the actual average composition is  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ , which is the nominal composition; it shows that the mercury/thallium content,  $\text{Tl}_{1.5}\text{Hg}_{0.4}$  per unit, remains rather constant from one crystal to the other; however, the Sr/Ca balance can vary significantly because, for an actual average  $\text{Sr}_{2.2}\text{Ca}_{0.8}$  content, local compositions such as  $\text{Sr}_2\text{Ca}_1$  and  $\text{Sr}_{2.6}\text{Ca}_{0.4}$  per unit have been observed in few crystals.

The overall [010] images shows that the stacking of the layers along the  $\bar{c}$  axis is perfectly ensured throughout the whole crystal, without any defect. The enlargement of such images allows the nature of the layers to be identified; in Figure 2, the positions of the cations are imaged as bright spots so that the four rows of very bright spots are correlated to the sequence  $[\text{SrO}] - [(\text{Tl}, \text{Hg})\text{O}] - [(\text{Tl}, \text{Hg})\text{O}] - [\text{SrO}]$  according to the 2212 structure (Figure 3); between these four rows, three rows of smaller dots are sandwiched, which are correlated to the  $[\text{CuO}_2] - [\text{Sr}, \text{Ca}] - [\text{CuO}_2]$  layers, in agreement with the 2212 mode (the different layers are identified on the micrograph).

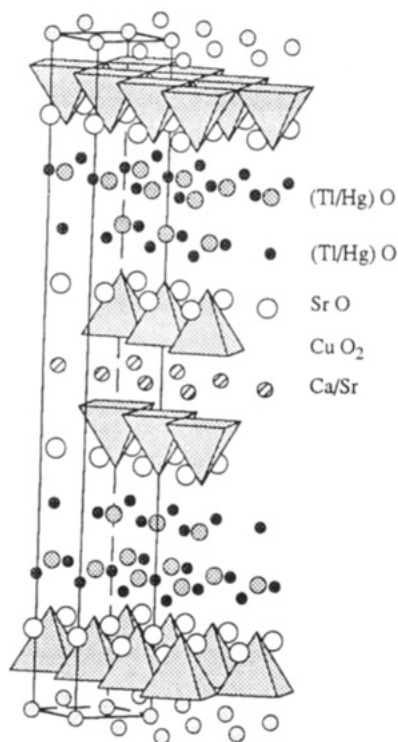
The cell parameters have been refined from the XRD data to  $a = 3.7935(1)$  Å and  $c = 28.514(1)$  Å. To confirm

(13) Rodriguez-Carjaval, J.; Proc. Satellite Meeting on Powder Diffraction of the XVth Congress of Int. Union of Crystallography, Toulouse, France, July 1990.

(14) Martin, C.; Maignan, A.; Provost, J.; Michel, C.; Hervieu, M.; Tournier, R.; Raveau, B. *Physica C* **1990**, *168*, 8.



**Figure 2.** Enlarged [010] image of the 2212 thallium mercury cuprate,  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ ; the nature of the layers is identified in the image. In that example, the cation positions are imaged as bright dots. The [010] ED pattern is in insert.



**Figure 3.** Idealized structure of the 2212 thallium mercury cuprate; the intermediate layers are mixed layers, [(Tl/Hg)O].

the structural type and the possibility of partial substitution of strontium for calcium, a structural study was undertaken. The different cations were located on the classical crystallographic sites of the 2212 structure (space group  $I4/mmm$ ). Owing to the similar scattering factors for thallium and mercury, only thallium occupancy on the Tl site was considered; in the same way, only calcium was considered on the calcium site. The positional parameters and isotropic thermal factors of the cations were refined and the occupancy factors of

**Table 1.** The Cuprates  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$  (1212) and  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$  (2212): Refined Parameters Obtained from the Powder X-ray Diffraction Data

	structure	
	1212	2212
lattice constants		
$a$ (Å)	3.7968(2)	3.7935(1)
$c$ (Å)	12.1357(7)	28.514(1)
space group	$P4/mmm$	$I4/mmm$
number of $hkl$	77	96
Tl		
$x$	0	0.5
$y$	0	0.5
$z$	0	0.21218(7)
$B$ (Å <sup>2</sup> )	1.5(1)	0.3(1)
$\tau$	0.89(1)	0.96(1)
Sr		
$x$	0.5	0
$y$	0.5	0
$z$	0.2117(3)	0.1218(1)
$B$ (Å <sup>2</sup> )	0.9(1)	1.0(1)
Ca		
$x$	0.5	0
$y$	0.5	0
$z$	0.5	0
$B$ (Å <sup>2</sup> )	0.1(3)	0.1(4)
$\tau$	1.43(2)	1.30(2)
Cu		
$x$	0	0.5
$y$	0	0.5
$z$	0.3624(4)	0.0584(2)
$B$ (Å <sup>2</sup> )	0.1(2)	0.1(1)
O(1)		
$x$	0	0
$y$	0.5	0.5
$z$	0.368(1)	0.0528(5)
O(2)		
$x$	0	0.5
$y$	0	0.5
$z$	0.164(2)	0.1441(8)
O(3)		
$x$	0.5	0
$y$	0.5	0
$z$	0	0.21218(7)
$R$ fact		
$R_p$	0.093	0.095
$R_{wp}$	0.120	0.122
$R_i$	0.086	0.080

Tl and Ca crystallographic sites. For oxygens, only positional parameters were refined, the  $B$  factors being arbitrarily fixed to  $1 \text{ \AA}^2$ . Moreover, the  $z$  value of the oxygen belonging to the TlO plane was constrained to be equal to  $z_{\text{Tl}}$ .  $\text{CaHgO}_2$  and  $\text{Sr}_4\text{Tl}_2\text{O}_6\text{CO}_3$ , present as impurities, were introduced as secondary phases. After successive refinements of the different variables, the different  $R$  factors were stabilized to  $R_p = 0.095$ ,  $R_{wp} = 0.122$  and  $R_i = 0.080$ , for the values given in Table 1.

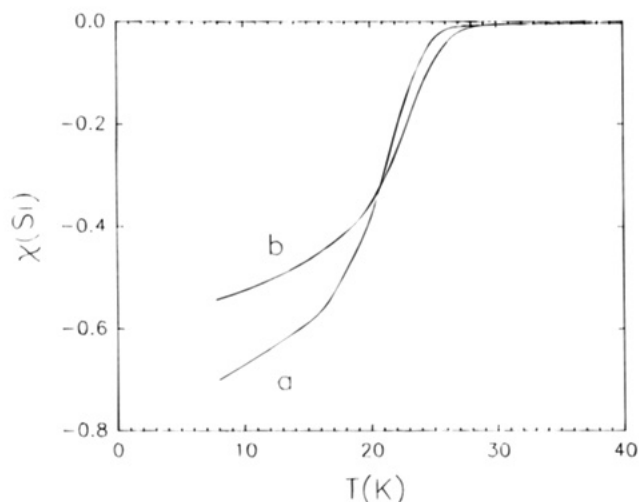
The refined occupancy factor of the calcium site ( $\tau = 1.30$ ) corresponds to 23.4 electrons instead of 18. Considering a partial occupancy by strontium, this leads to  $\text{Sr}_{0.3}\text{Ca}_{0.7}$  which remains close to the nominal composition ( $\text{Sr}_{0.2}\text{Ca}_{0.8}$ ) and agrees with the EDS analysis. The calculated interatomic distances are listed in Table 2; they are close to those observed in the strontium based cuprate  $\text{Tl}_2\text{Sr}_2\text{CuO}_6$ <sup>15</sup> except for the Tl–O(2) distance (1.94 Å) which is rather shorter than in thallium cuprates (2.00–2.06 Å). The latter phenomenon could be due to the presence of mercury which involves shorter distance along the  $c$  axis. The Cu–O interatomic

(15) Martin, C.; Maignan, A.; Huvé, M.; Michel, C.; Hervieu, M.; Raveau, B. *Eur. J. Solid State Inorg. Chem.* **1993**, *30*, 7.

**Table 2. The Cuprates  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$  (1212) and  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$  (2212): Selected Interatomic Distances**

M-O	1212		2212	
	$d$ (Å)	$\times n$	$d$ (Å)	$\times n$
Tl-O(2)	1.99(2)	$\times 2$	1.94(2)	$\times 1$
Tl-O(3)	2.685(1)	$\times 4$	2.682(1)	$\times 4$
Tl-O(3)			2.157(3)	$\times 1$
Sr-O(1)	2.69(1)	$\times 4$	2.73(1)	$\times 1$
Sr-O(2)	2.747(4)	$\times 4$	2.757(6)	$\times 4$
Sr-O(3)	2.570(3)	$\times 1$	2.576(4)	$\times 1$
Ca-O(1)	2.480(9)	$\times 8$	2.421(8)	$\times 8$
Cu-O(1)	1.900(1)	$\times 4$	1.904(1)	$\times 4$
Cu-O(2)	2.41(2)	$\times 1$	2.44(3)	$\times 1$
Cu-Cu <sup>a</sup>	3.341(6)		3.330(7)	
O(1)-O(1) <sup>a</sup>	3.20(2)		3.01(2)	

<sup>a</sup> Distances along the  $c$  axis.



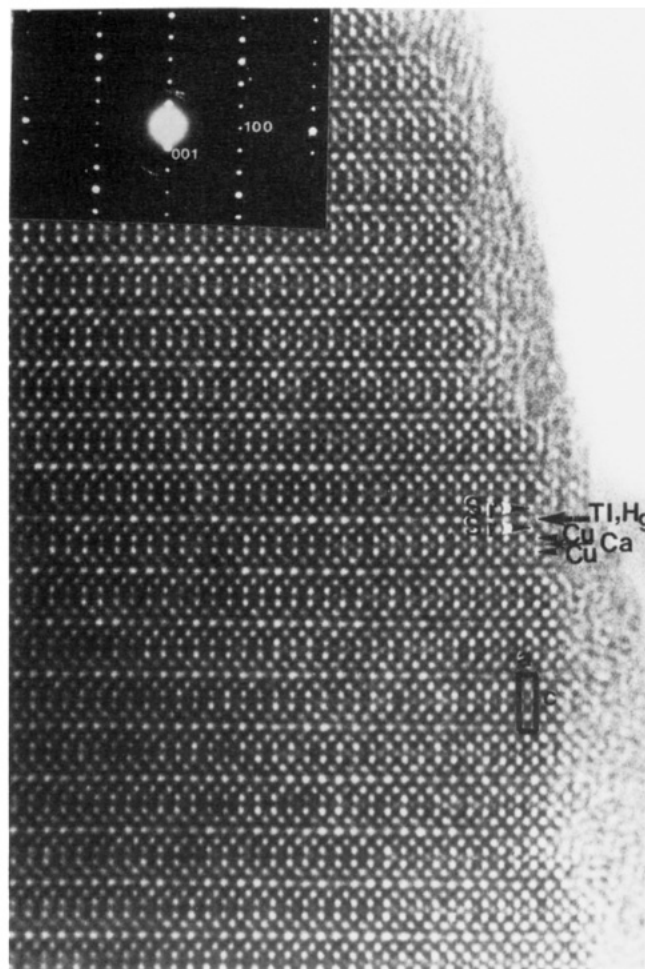
**Figure 4.** Temperature dependence of the susceptibility  $\chi'$  ( $T$ ) for  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ : as synthesized (a) and after an Ar/ $\text{H}_2$  annealing (b).

distances are smaller than that observed in the barium based 2212 cuprate,  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ ,<sup>20,21</sup> in agreement with the Ba and Sr ionic radii.

The susceptibility measurements show that this 2212 strontium based cuprate is a 25 K superconductor with a high diamagnetic volume fraction and a sharp transition (Figure 4, curve a). The critical temperature does not vary with the nominal oxygen content ( $y = 0, 1$ , and 2) but the diamagnetic volume fraction increases with  $y$ . Attempts to improve superconductivity by annealings, at different temperatures and under different atmospheres, failed; a decrease of the diamagnetic volume fraction is observed (see curve b for annealing under an hydrogenated argon flow at 310 °C) whereas  $T_c$  remains nearly constant. These results suggest that the oxygenated as-synthesized sample is optimized.

The critical temperature is considerably lower than that observed in the barium-based 2212 cuprates which is close to 123 K for the optimized samples.<sup>14</sup> Compared to the 2201 oxides  $\text{Tl}_2\text{Ba}_{2-x}\text{Sr}_x\text{CuO}_6$ ,<sup>15</sup> where  $T_c$  decreases with  $x$ , up to the formation of a nonsuperconducting strontium based compound ( $x = 2$ ), such an effect can be mainly attributed to the role of strontium.

**1212  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$  Cuprate.** For the nominal composition  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{8.5}$ , a 1212 phase is synthesized. The electron diffraction study confirms the cell parameters and the absence of extra reflections or streaks in the ED patterns as shown from

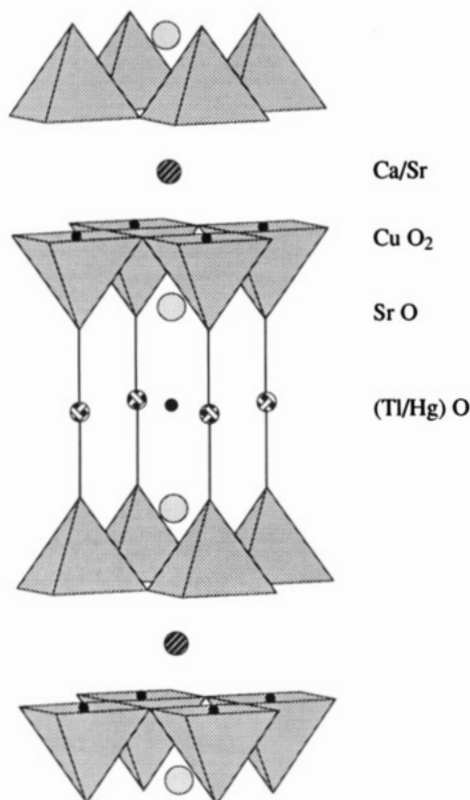


**Figure 5.** Enlarged [010] image the 1212 thallium mercury cuprate,  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$ . The positions of the cations are imaged as bright dots; the nature of the layers is indicated on the right part of the micrograph. Most of the crystals exhibit a perfect sequence of the layer stacking, according to a 1212 mode. The [010] ED pattern is shown in insert.

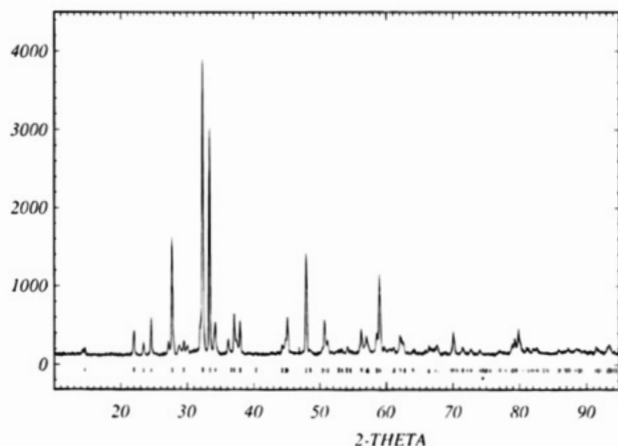
the [010] pattern (insert in Figure 5). High-resolution images confirm the 1212-type layer stacking sequence along the  $c$  direction. An example is shown in Figure 5, where the positions of the cations are imaged as bright dots, the three rows of brightest spots are correlated to the sequence [SrO]–[(Tl,Hg)O]–[SrO], characteristic of the 1212 structure (Figure 6), and the smallest ones to the [CuO<sub>2</sub>]–[(Ca,Sr)O]–[CuO<sub>2</sub>] as observed in the 2212 and 1212 compounds. The nature of the different layers is indicated on the right part of the image. Note that most of the crystals exhibit highly regular stackings of the layers along the  $c$  axis. The EDS analyses evidence that the mercury content,  $x$ , in the intermediate layer, [Tl<sub>1-x</sub>Hg<sub>x</sub>O], is constant and close to 0.2; the Sr/Ca ratio can significantly vary, as observed in the 2212's, since calcium content as low as 0.3 have been observed in some crystals.

The cell parameters are refined from the XRD data (Figure 7) to  $a = 3.7968(2)$  Å and  $c = 12.1357(7)$  Å. The parameter values are very close to those observed in the mercury-free cuprate ( $a = 3.794$  Å and  $c = 12.133$  Å).<sup>8</sup> The main difference between the two oxides resides in the electron diffraction patterns, the mercury-free compound exhibiting systematically extra reflections as a result of complex order-disorder phenomena.<sup>8</sup> Struc-





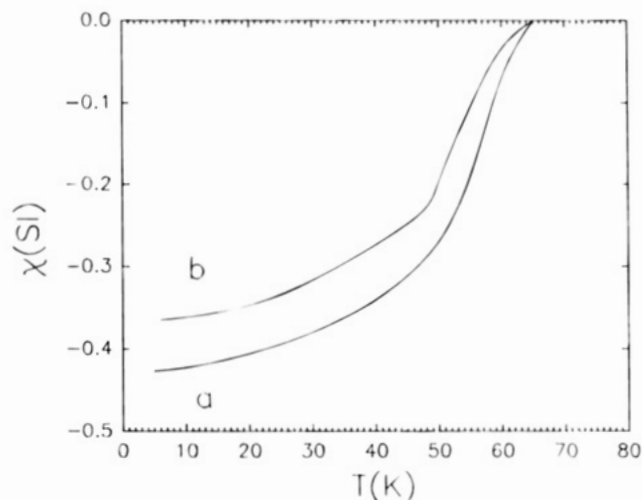
**Figure 6.** Idealized structure of the 1212 thallium mercury cuprate; the intermediate layers are mixed layers  $[\text{Tl}_{0.8}\text{Hg}_{0.2}\text{O}]$ .



**Figure 7.** Powder X-ray diffraction pattern of  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$ . The marks correspond to the Bragg angle positions of the "1212" structure.

tural calculations were also performed for this compound. Following the same refinement procedure as for the 2212 member, the  $R$  factors were lowered to  $R_p = 0.093$ ,  $R_w = 0.120$ ,  $R_i = 0.086$ , for the refined values listed in Table 1.

The occupancy factor of the calcium site is slightly higher than that observed for the 2212 member and can be considered as the result of a partial occupancy by strontium and thallium; refining the "thallium" site evidences a significant electronic deficiency (69.5 electrons). Referring to the XRD and EDS results, the compositions  $\text{Tl}_{0.7}\text{Hg}_{0.2}\text{Sr}_2(\text{Sr}_{0.2}\text{Ca}_{0.7}\text{Tl}_{0.1})\text{Cu}_2\text{O}_{7-\delta}$  can be proposed for the 1212 cuprate.



**Figure 8.**  $\chi^2(T)$  curves of  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_2\text{O}_{7-\delta}$ : as synthesized (a) and after an Ar/H<sub>2</sub> annealing (b).

The interatomic distances are listed in Table 2. No drastic differences with those calculated for the 2212-type compound are observed.

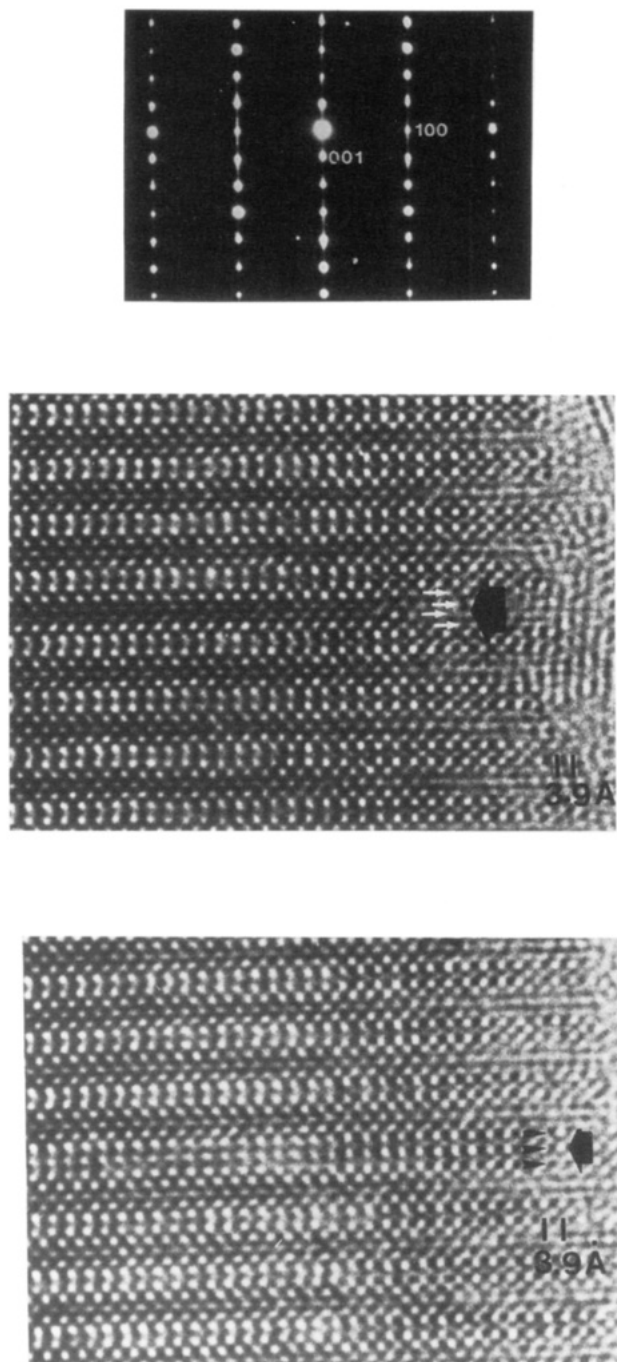
The susceptibility measurements (Figure 8) show a critical temperature of 65 K and a significant diamagnetic volume fraction.  $T_c$  is not modified by postsynthesis annealings, but the diamagnetic volume fraction is decreased. The critical temperature of these strontium-based 1212 cuprates is lower than that observed for the 1212 barium-based oxides.<sup>16</sup> However, compared to other thallium 1212 cuprates  $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-\delta}$  ( $T_c = 110$  K) and  $\text{TlBaSrCaCu}_2\text{O}_{7-\delta}$  ( $T_c = 100$  K), strontium does not seem to influence so dramatically the critical temperature since only a smooth decrease is observed. The comparison with other oxides which exhibit only SrO layers,  $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Sr}_2\text{CaCu}_2\text{O}_{7-\delta}$ <sup>11</sup> with a  $T_c$  of 85 K and  $\text{TlSr}_2\text{CaCu}_2\text{O}_{7-\delta}$  with a  $T_c$  (offset) of 47 K and a  $T_c$  (onset) of 60 K, suggests that the composition of the intermediate layer and the way it can modify the charge balance are the most important parameters.

**Intermediate Compositions: Intergrowths of 1212 and 2212 Members.** To check the way (Tl–Hg) nonstoichiometry is accommodated in the matrices, intermediate compositions,  $(\text{Tl}_{0.8}\text{Hg}_{0.2})_{2-z}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-1.4z}$ , have been investigated, with  $z$  ranging from 0.5 to 0.9 by step of 0.1.

For low  $z$  values ( $z = 0.1$  and  $z = 0.2$ ), 2212's members are preferentially formed, and for high  $z$  values ( $z = 0.3$  and  $z = 0.4$ ) the 1212's is the majority phase. The XRD patterns show the formation, respectively, of 2212's or 1212's or mixtures of the two members. The electron diffraction study, performed on numerous crystals of the different samples, shows that a majority of crystals is characterized by the presence of extra reflections and streaks along the  $c^*$  axis; these features are observed as well in the 2212 as in the 1212 lattices, depending on the nominal composition, and are correlated to the existence of order-disorder phenomena. The nature of the defects can be identified from the HREM images; they mainly correspond to the stacking of defective members along  $c$ .

When the streaks are weak and diffuse (Figure 9a), only some defective members are formed in the matrix; an example of 1212 matrix is shown in Figure 9b,c; in both images, the rows of cations are imaged as rows of bright spots. The first defect (Figure 9b) corresponds

(16) Morosin, B.; Ginley, D. S.; Hlava, P. F.; Carr, M. J.; Baughman, R. J.; Schirber, J. E.; Venturini, E. L.; Kwak, J. F. *Physica C* **1988**, *152*, 413.

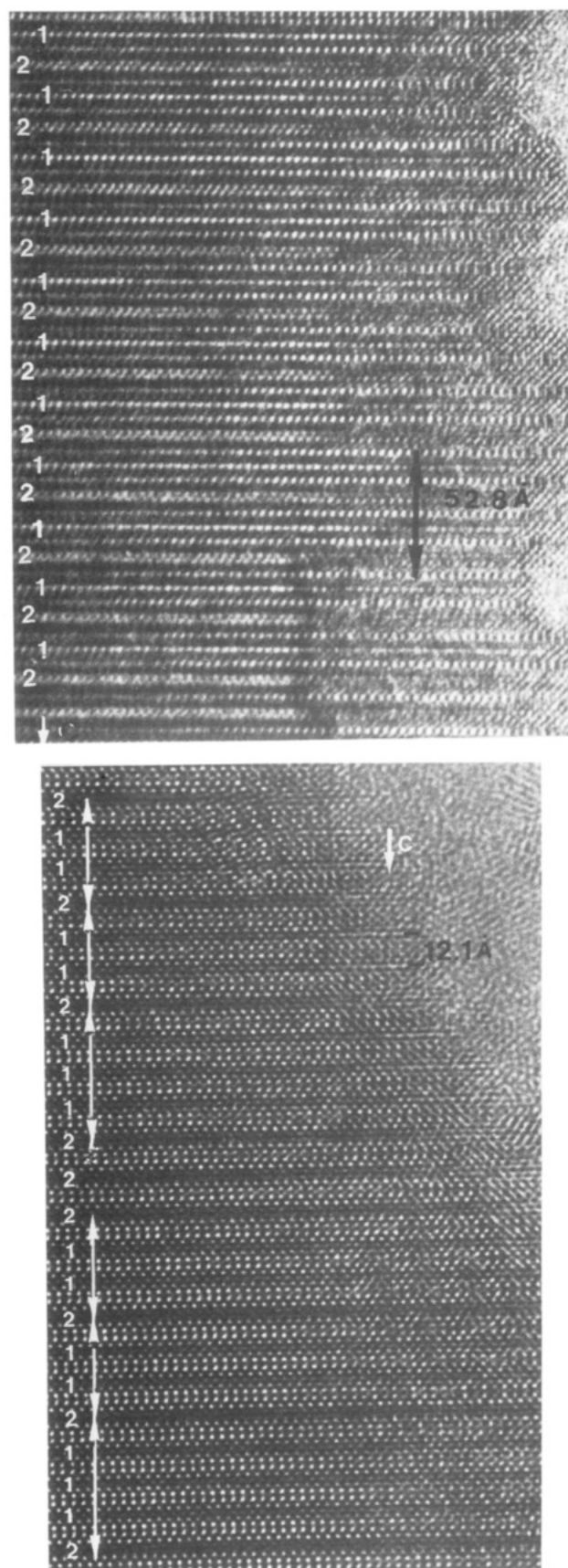


**Figure 9.** (a, top) Example of [010] ED patterns recorded for the intermediate compositions enlarged it exhibits streaks along  $c^*$  but the strong reflections are those of the 1212 system. (b, middle) [010] image of a 2212 defective members observed in a 1212 matrix 2212. (c, bottom) 1223 defective member.

to a defective member with a typical 2212 stacking, whereas the second defect (Figure 9c) is characterized by the existence of an additional perovskite layer and corresponds to a local 1223 member. The latter defect is, by far, less frequent than the other ones.

Another type of distribution corresponds to local orderings of both cuprates, so that new complex members are formed which all belong to a large family,  $[2212]_m [1212]_n$ . Some of these "new members" which are formed according to that building principle are most frequently observed:

(i) 1212's and 2212's alternate regularly (Figure 10a); in that case, a new phase corresponds to  $m = 1$  and  $n =$



**Figure 10.** Examples of the formation of local intergrowths between the 2212 and 1212 members: (a) term  $[1-1]$  and (b) terms  $[1-1]$ ,  $[1-2]$ , and  $[1-3]$  of the family  $[2212]_m [1212]_n$  exhibited mixed  $[Tl_{0.8}Hg_{0.2}O]$  intermediate layers.

$[1-1]$ , termed  $[1-1]$ , is stabilized which consists in the regular intergrowth of single and double  $(Tl_{0.8}Hg_{0.2}O)$  layers, separated by double perovskite layers. Similar

intergrowths have been previously reported in the mercury free cuprates.<sup>17-22</sup>

(ii) One observes also areas where 2212's alternate with one, two, or three 1212's and areas where 1212's occurs every two, three, or four 2212's. In the first case, such areas results from an aleatory distribution of [1-1], [1-2] and [1-3] members, an example is shown in Figure 10b. In the second case, we can consider that it corresponds to an aleatory distribution of [1-1], [2-1], [3-1], and [4-1] members.

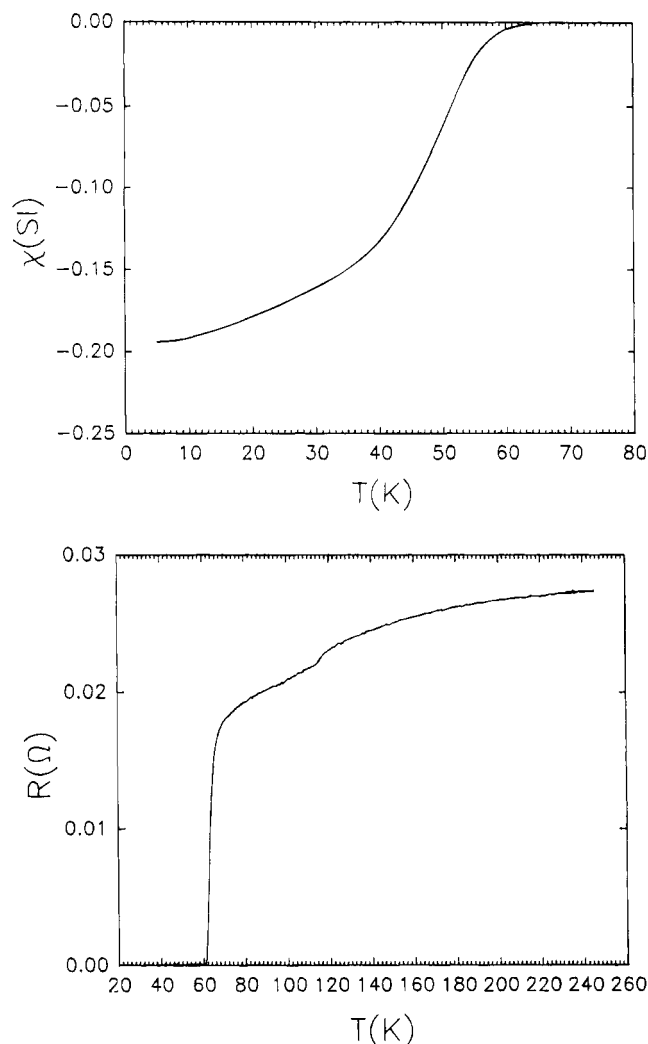
The stabilization of complex members corresponding to low values of  $m$  and  $n$ , in phases built from the intergrowth of two structural units, has often been observed as a stating of fact. Different attempts have been made to synthesize these first members in the form of single phases; the XRD and ED patterns show that they are formed but always coexist in the bulk.

The formation of intergrowths between the 1212 and 2212 members is in agreement with the nominal compositions since the (Tl + Hg) content ranges from 2 (corresponding to the 2212's) to 1 (corresponding to the 1212's). Such behavior has been observed in the thallium-deficient 2212 superconductor  $\text{Tl}_{2-x}\text{Ba}_2\text{CaCu}_2\text{O}_{8-\delta}$  with  $x \approx 0.4$ ,<sup>21</sup> where intergrowths of 2212 and 1212 members and localized modulations of the rock salt layers were observed by HREM. Similar modulations have been observed in the thallium/mercury-deficient compounds, they can be considered as a sign of thallium deficiency in the intermediate layers. In the mercury-doped sample, they arise in areas where the matrix exhibits double rock salt layers, i.e., 2212's, but extend only on very small areas, few angstroms long.

The susceptibility measurements have been performed for these deficient materials;  $T_c$ 's range from 40 to 65 K (depending of the  $z$  value), and the transitions are rather broad. An example is shown in Figure 11a for a sample of nominal composition  $\text{Tl}_{1.3}\text{Hg}_{0.3}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{7.25+\delta}$ . The resistivity curve of the sample (Figure 11b) confirms the  $T_c$  onset of 62 K and the metallic behavior of the sample; the small variation observed at 120 K is supposed to be correlated to the existence of 1223 defective members in the matrix, as observed by HREM.

### Conclusion

These results show the possibility to stabilize layered cuprates of the TSCC system by substituting partially mercury for thallium, the maximum Hg content in the thallium monolayers or bilayers remaining low, i.e., smaller than 0.2 per thallium site. The first remarkable feature deals with the synthesis, for the first time, of a "Tl-Sr" superconducting cuprate involving thallium bilayers. The second important point deals with the



**Figure 11.**  $\chi'(T)$  curve for a sample of nominal composition  $\text{Tl}_{1.3}\text{Hg}_{0.3}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$  (a, top) and corresponding  $R(T)$  curve (b, bottom).

cationic ratio Sr/Ca, which implies Sr for Ca substitution on the calcium sites. The large nonstoichiometry, involving complex intergrowths and possible formation of cationic vacancies, is the third original characteristic of these oxides that exhibit an extraordinary flexibility of their thallium-oxygen layers.

From the viewpoint of superconductivity, the critical temperature of 25 K observed for the 2212 cuprate  $\text{Tl}_{1.5}\text{Hg}_{0.4}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8-\delta}$ , if it appears rather low, can be considered as exceptional. The latter phase is indeed in TSCC-based systems, the only superconductor with thallium bilayers that has been isolated up to date. The critical temperature of 65 K obtained for the 1212 cuprate to  $\text{Tl}_{0.8}\text{Hg}_{0.2}\text{Sr}_{2.2}\text{Ca}_{0.7}\text{Cu}_{2.1}\text{O}_{7-\delta}$ , compared to that observed for multiphasic samples with the composition  $\text{TlSr}_2\text{CaCu}_2\text{O}_{7-\delta}$ ,<sup>6,8</sup> ranging from 50 to 70 K, shows that the substitution of mercury for thallium does not influence dramatically the superconducting properties of this oxide. The transitions observed for intermediate compositions, corresponding to  $T_c$ 's ranging from 30 to 65 K, although they are broad, are of interest, since they suggest the possibility to isolate other superconductors in the TSCC-based systems.

CM940552E

(17) Verweft, M.; Van Tendeloo, G.; Amelinckx, S. *Physica C* **1988**, *156*, 609.

(18) Zandbergen, H. W.; Van Tendeloo, G.; Van Landuyt, J.; Amelinckx, S. *Appl. Phys. A* **1988**, *46*, 233.

(19) Maignan, A.; Michel, C.; Hervieu, M.; Martin, C.; Groult, D.; Raveau, B. *Mod. Phys. Lett. B* **1988**, *2*, 681.

(20) Iijima, S.; Ichihashi, T.; Shimakawa, Y.; Makano, T.; Kubo, Y. *Jpn. J. Appl. Phys. Lett.* **1988**, 1054.

(21) Michel, C.; Martin, C.; Hervieu, M.; Maignan, A.; Provost, J.; Huvé, M.; Raveau, B. *J. Solid State Chem.* **1992**, *96*, 271.

(22) Hewat, A. W.; Hewat, E. A.; Brynestad, J.; Mook, H. A.; Specht, E. D. *Physica C* **1988**, *152*, 438.