PHYSICAL REVIEW B VOLUME 45, NUMBER 10 1 MARCH 1992-II

Superconductor-to-metal transition caused by oxygen nonstoichiometry in $TlSr_2CaCu_2O_{7-\delta}$ having a Cu-O pyramidal layer

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(Received 5 March 1991; revised manuscript received 7 November 1991)

A transition from a 68-K superconductor to an overdoped nonsuperconducting metal has been observed in $TlSr_2CaCu_2O_{7-\delta}$ having a Cu-O pyramidal layer. This reversible transition is caused by a small change (~ 0.08) in oxygen deficiency δ, without showing a significant change in the crystal structure. The Hall measurements demonstrate that the superconductivity is suppressed by overdoping of hole carriers. No significant changes of the Hall coefficient or the magnetic susceptibility are observed at the superconductor-metal phase boundary, suggesting a similarity and continuity between both the electronic structures. These features are quite similar to those for another overdoped system: $Tl_2Ba_2CuO_{6+\delta}$ with a Cu-O octahedral layer.

I. INTRODUCTION

An important fact about high-T_c superconductivity (HTSC) is that it appears only in a narrow composition range between an antiferromagnetic (AF) insulator and a normal metal. Although a compositional change is generally accompanied with some structural changes such as ordering or local atomic displacements, this fact still strongly suggests that carrier concentration is a crucial factor for the occurrence of HTSC. One plausible picture for HTSC is appropriate carrier doping of an AF background. In this context many theoretical and experimental studies so far have been focused on the AF-insulator-to-superconductor transitions induced by the carrier doping. Less attention has been paid to the superconductor-to-normal-metal transitions arising from overdoping of carriers. This is partly because it has been difficult for most materials to be overdoped enough to suppress the superconductivity completely. However, considering that HTSC lies in an ambiguous region between two well-defined categories of a strongly correlated AF insulator and a normal metal, an investigation based on an approach from the metallic side should be as important as that from the insulating side. In particular, it is very important to clarify whether any singularities exist at the superconductor-metal phase boundary, because it gives us some information concerning the continuity or discontinuity between HTSC and the normal Fermi liquid.

One material that showed a superconductor-metal transition upon doping was $La_{2-x}Sr_xCuO_4$,[1] which changed from an insulator to a normal metal via a 40-K superconductor as x increased. Transport properties clearly indicated the hole doping by Sr- substitution.[2] The second material was $TlLa_{1-x}Ba_{1+x}CuO_5$,[3] where a very similar composition dependence of T_c was observed with increasing x. Recently, we have found a third material $Tl_2Ba_2CuO_{6+\delta}$ (see Fig. 1), which is gradually changed from a 85-K superconductor to a nonsuperconducting metal by overdoping hole carriers through excess oxygen introduced to an interstitial site between double TlO layers.[4–8] It is noted that these three materials have a Cu-O octahedron layer. This implies that the octahedron structure is most suitable for the hole doping, which is quite reasonable because two apical oxygen ions with negative charges will stabilize the positive hole carriers between them.

On the other hand, for a Cu-O pyramidal layer structure, a complete suppression of superconductivity by overdoping has never been realized, although small suppressions were observed in several materials such as $YBa_2Cu_3O_7$,[9] $Tl_2Ba_2CaCu_2O_8$,[6] and $Bi_2Sr_2CaCu_2O_8$.[10] However, recent reports on $TlSr_2CaCu_2O_7$ and its substituted compounds,[11–13] which have two Cu-O pyramidal layers between Tl-O monolayers as shown in Fig. 1, suggested that this structure could be overdoped to the level of a normal metal. These reports were, however, in contrast to previous studies[14–16] in which only a mixed phase and/or a superconductor with T_c above 50 K was obtained. We have intensively examined the preparation method and finally confirmed that we can obtain an almost-single-phase $TlSr_2CaCu_2O_7$ showing a metallic but nonsuperconducting behavior.

Moreover, we have observed that metallic nonsuper-

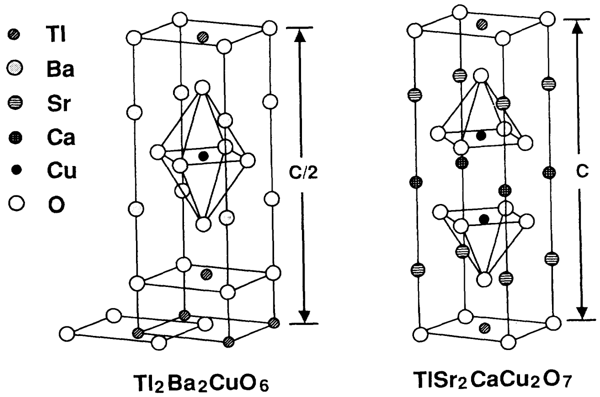

FIG. 1. Crystal-structure models for $Tl_2Ba_2CuO_6$ and $TlSr_2CaCu_2O_7$.

conducting $TlSr_2CaCu_2O_7$ is gradually changed to a 68-K superconductor if it is reduced in an argon atmosphere. Weight measurements reveal that this transition is reversibly caused by release and incorporation of a small amount of oxygen ($\sim$0.08 per formula unit). Recent neutron-diffraction measurements on our samples suggest that the oxygen site of the Tl-O layer is somewhat deficient and is responsible for this transition.[17] The Hall measurements clearly show that the hole carriers are increased when T_c is lowered by the incorporation of oxygen. Therefore, $TlSr_2CaCu_2O_{7-\delta}$ is demonstrated to have a Cu-O pyramidal layer and to show a superconductor-metal transition due to overdoping.

In this paper we show how the structure and physical properties of $TlSr_2CaCu_2O_{7-\delta}$ are changed through overdoping of hole carriers. It is noted that no significant changes of the crystal structure, Hall coefficient, or magnetic susceptibility are observed at the superconductor-metal phase boundary, which suggests a similarity and continuity between both the electronic structures. These features are in sharp contrast to those for overdoped $La_{2-x}Sr_xCuO_4$,[2,18] but are quite similar to those for $Tl_2Ba_2CuO_{6+\delta}$,[7,8] having a Cu-O octahedral layer.

II. SAMPLE PREPARATION

$TlSr_2CaCu_2O_{7-\delta}$ samples were prepared using a conventional powder method. Tl_2O_3, SrO, CaO, and CuO powders were mixed, pressed into a pellet, sealed in a gold crucible, and sintered in oxygen at about 900 °C for several days with several intermediate grindings. It should be noted that the sample quality is very sensitive to the preparation conditions such as sintering temperature, probably because of the large volatility of Tl, and

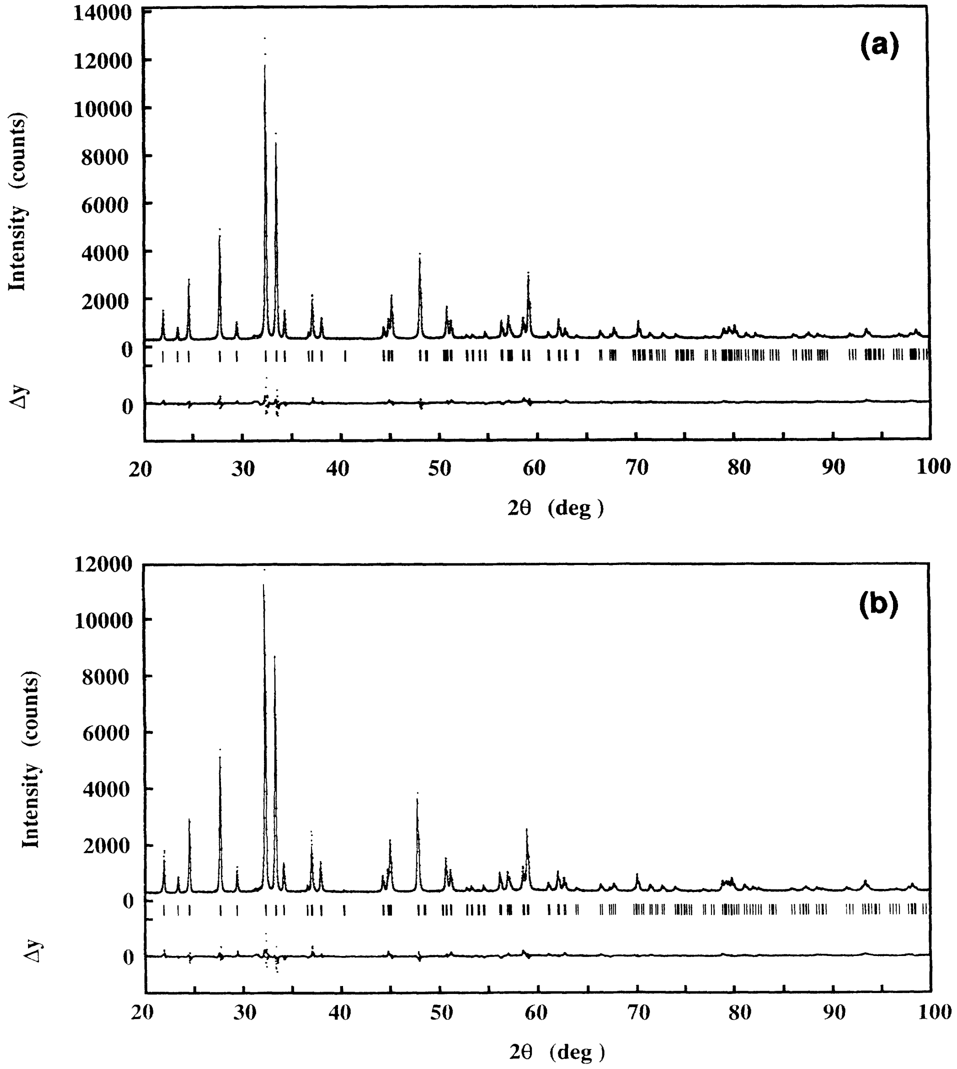

FIG. 2. Rietveld-refinement patterns for $TlSr_2CaCu_2O_{7-\delta}$: (a) oxygen-annealed sample with $\delta=0.12$ and $T_c<2$ K and (b) argon-annealed sample with $\delta=0.20$ and $T_c=68$ K. Dots are observed intensities, and solid lines are calculated intensities. Vertical marks below the profile indicate the positions of the allowed reflections. The curve at the bottom is the difference between the observed and calculated intensities in the same scale.

the details will be described elsewhere. The crystal structure was examined by x-ray diffraction using Cu $K\alpha$ radiation. As shown in Fig. 2, all peaks of the x-ray-diffraction pattern could be assigned to those for the crystal-structure model (tetragonal space group $P4/mmm$) presented in Fig. 1, except for a very small unknown one at $2\theta=31.2°$. The Rietveld refinement using the program RIETAN (Ref. 19) showed an excellent fit with a residual factor $R_{\mathrm{wp}}=7.2\%$ ($R_{\mathrm{e}}=4.5\%$). All cation sites were fully occupied, while some local displacements of Tl in the *a*-*b* plane were suggested. Since the refined occupancy for the Ca site was considerably larger than unity, about 19% of the Ca site seems to be substituted by Tl.

III. OXYGEN NONSTOICHIOMETRY

The as-sintered samples were metallic and nonsuperconducting down to 2 K. However, they showed superconductivity after annealing in argon at 350–550 °C for 5 h. The higher T_c value was obtained as the annealing temperature was raised. The superconductivity again disappeared by annealing in oxygen at 350 °C for 10 h. These facts strongly suggest the significant role of the oxygen nonstoichiometry. We determined the relative change in oxygen content by measuring the weight change between the argon- and oxygen-annealed samples. The reversibility of the weight change was confirmed for all samples. The weight of oxygen-annealed sample was decreased by argon annealing, and it was almost completely recovered by reannealing in oxygen. Fig. 3 shows the relationship between T_c and the relative change in oxygen content, Δy, in the formula of $\mathrm{TlSr_2CaCu_2O}_y$ ($y \approx 7$). The error bars in Fig. 3 represent the ranges of experimental values measured on several samples of about 100 mg each. Because Δy is defined as the relative change in oxygen content from the oxygen-annealed state ($T_c < 2$ K), there is no error bar at $\Delta y=0$. The error bar for the vertical axis is not shown because the scattering of T_c values is rather small. The most sensitive factor in the Δy measurement seems to be small surface absorption of humidity. It is empirically estimated as $<10\ \mu$g for a sample of 100 mg if the measurement is done within 30 min after taking out the sample from the furnace. This uncertainty of $\sim 10\ \mu$g for a 100-mg sample corresponds to the uncertainty of Δy of ~ 0.004, which is comparable to the error bars in Fig. 3.

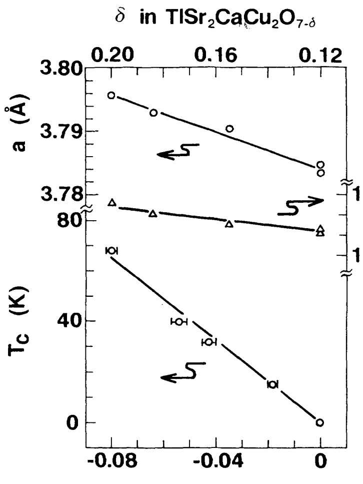

FIG. 3. T_c and lattice parameters *a* and *c* plotted against the oxygen content for $\mathrm{TlSr_2CaCu_2O}_{7-\delta}$. The lower horizontal axis shows the relative change in oxygen content, Δy, measured from the oxygen-annealed state. The upper horizontal axis shows the δ values ($\delta=0.12-\Delta y$) based on the neutron-diffraction study (Ref. 17).

As shown in Fig. 3, T_c is almost linearly increased with decreasing the oxygen content, which is quite similar to the result for $\mathrm{Tl_2Ba_2CuO}_{6+\delta}$.[6] The maximum T_c value obtained in the present study was 68 K. However, we should note that this structure shows higher T_c values of ~ 90 K if the carrier concentration is reduced by Y substitution for Ca. This suggests that the optimum carrier concentration for this structure, at which T_c becomes maximum, has not been achieved by the present argon reduction. According to the recent neutron-diffraction study on our samples,[17] some oxygen deficiency is detected on the Tl-O layer. The oxygen site occupancy of the Tl-O layer changes from 0.877 ± 0.018 for $T_c<2$ K to 0.801 ± 0.015 for $T_c=58$ K, resulting in $\Delta y=-0.076$ for $T_c=58$ K. This result shows a very good agreement with the results of weight measurement ($\Delta y=-0.071$ for $T_c=58$ K) presented in Fig. 3. Therefore, we fix the oxygen deficiency δ for the oxygen-annealed sample to 0.12 in this paper, that is, $\delta=0.12-\Delta y$. This δ value is also shown on the upper horizontal axis in Fig. 3.

Figure 3 also shows subtle but systematical changes in the lattice parameters *a* and *c*, determined by the Rietveld refinement. We determined the Δy values for these samples by measuring both T_c values and weight losses in argon annealing, which were consistent with the T_c-Δy relationship in Fig. 3. Two data points at $\Delta y=0$ represent the results for two different samples, both of which are oxygen annealed and nonsuperconducting down to 2 K. At present, the origin of the small differences in *a* and *c* values between both samples is unclear. However, it should be noted that such small differences could be caused by some kinds of defects such as Tl substitution for Ca. In any case the overall dependence of the lattice parameters on the oxygen content is much more significant and systematical than the difference between both samples at $\Delta y=0$. As shown in Figs. 2(a) and 2(b), the Rietveld refinement shows an excellent fit for all δ's, and no evidence of phase separation or phase transformation is detected. These facts assure the sample homogeneity for all δ's.

The sample homogeneity is also suggested by the sharp and single transition in the Meissner signal as shown in Fig. 4. All data in Fig. 4 are obtained on the same sintered sample whose T_c was repeatedly changed by annealing. The demagnetization effect was ignored because the estimated demagnetization factor was as small as 0.1. The relatively small ratio ($<20\%$) of the Meissner signal to the perfect diamagnetism (the Meissner fraction) is

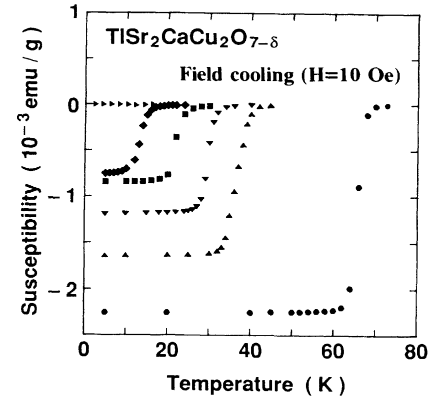

FIG. 4. Meissner signals measured under the constant field of 10 Oe for $TlSr_2CaCu_2O_{7-\delta}$ with various T_c's. The δ values are 0.12 (▶), 0.138 (♦), 0.15 (■), 0.163 (▼), 0.175 (▲), and 0.20 (●).

considered to be due to the flux pinning,[20] because the shielding effect at 5 K shows nearly perfect diamagnetism for all samples in Fig. 4. It is also confirmed that a powdered sample with T_c of 68 K shows a much larger Meissner fraction of 50%, which assures bulk superconductivity and suggests the significant effect of flux pinning in a sintered sample.

IV. PHYSICAL PROPERTIES

Fig. 5 shows the temperature dependences of the resistivity ρ, Hall coefficient R_H, and Hall number $n_H = 1/R_H e$ for samples with different δ's, which were measured by the van der Pauw method using a disk sample of about 10-mm diam.×0.2-mm thick under a magnetic field of up to 8 T. All of the data in Fig. 5 were taken on the same sample whose T_c was repeatedly changed by annealing in argon or oxygen. Both the resistivity and positive Hall coefficient are decreased with increasing oxygen content, which clearly demonstrates the hole doping by oxygen. The Rietveld refinement suggests that the hole carriers are mainly doped to the CuO_2 layer, because the Sr and Ca ions with positive charges go away from the CuO_2 layer with hole doping, while the apical oxygen ion approaches it. The temperature dependence of the resistivity is fitted well by a power-law dependence $\rho = \rho_0 + T^n$ for all δ's. The exponent n is gradually increased from 1.3 to 1.7 with doping. These results are difficult to explain in terms of electron-phonon scattering, but are very similar to those for $Tl_2Ba_2CuO_{6+\delta}$.[8] The Hall coefficient R_H shows a broad maximum at 100–140 K for all δ's, above which it is slowly decreased so that the Hall number $n_H = 1/R_H e$ shows a linear temperature dependence. It is interesting that even the metallic sample (A) still shows a linear temperature dependence of n_H, which is a common behavior in HTSC's, but incompatible with a simple Fermi-liquid description. These features are also very similar to those for $Tl_2Ba_2CuO_{6+\delta}$.[8] It should be noted that R_H is always positive and only gradually decreased upon doping without showing any anomalies at the superconductor-metal phase boundary. This is quite similar to the result for $Tl_2Ba_2CuO_{6+\delta}$,[8] but is in sharp contrast to that for overdoped $La_{2-x}Sr_xCuO_4$,[2] where R_H decreases rapidly with doping and finally changes sign and becomes negative. We believe that the present results of transport properties on polycrystalline samples mainly reflect the in-plane properties because of the large electrical anisotropy. This situation was found to be appropriate for other high-T_c Cu oxides.[2,8] Moreover, the relatively small values of both the resistivity and R_H suggest that the effect of grain

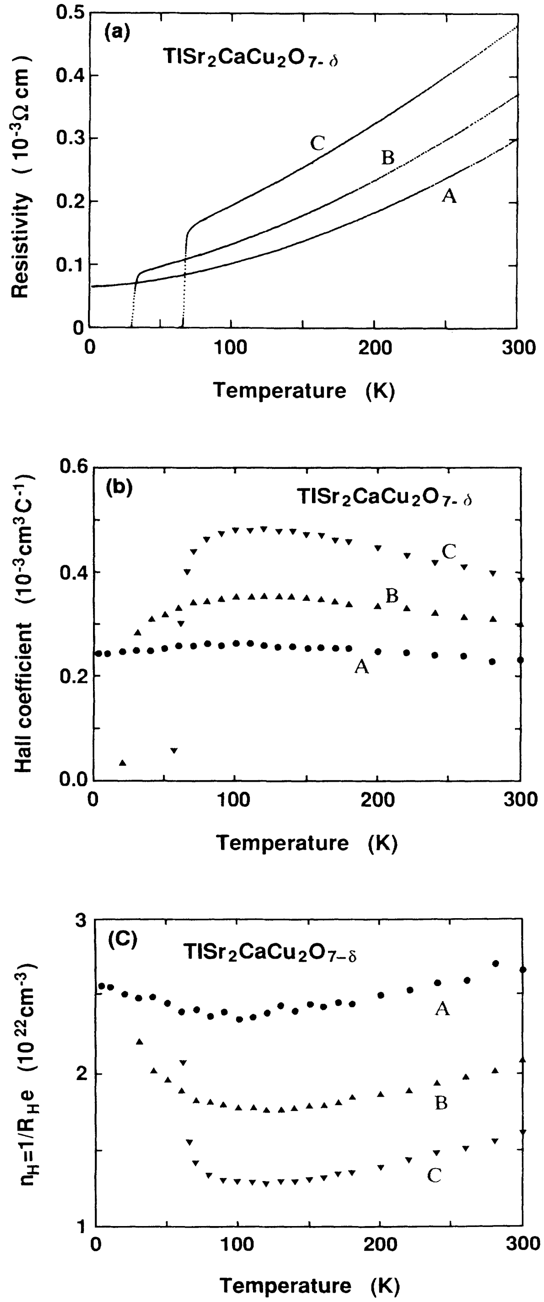

FIG. 5. Temperature dependences of (a) resistivity, (b) Hall coefficient, and (c) Hall number for $TlSr_2CaCu_2O_{7-\delta}$ with various δ's. The δ (T_c) values for samples A, B, and C are 0.12 (< 2 K), 0.16 (30 K), and 0.20 (68 K), respectively.

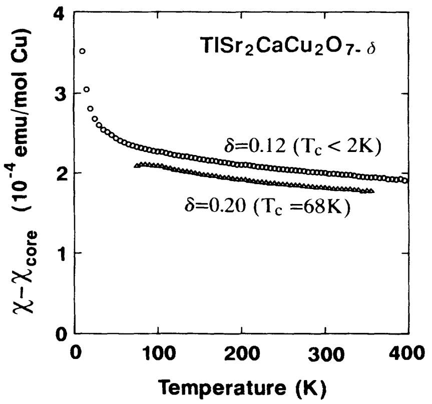

FIG. 6. Temperature dependence of the magnetic susceptibility after correcting the core diamagnetism χ_{core} for $TlSr_2CaCu_2O_{7-\delta}$ with $\delta=0.12$ ($T_c<2$ K) and $\delta=0.20$ ($T_c=68$ K).

boundaries is not significant in this sample.

The temperature dependence of normal susceptibility χ was measured at 1 T. Fig. 6 shows the data after correcting the core diamagnetism $\chi_{core}=-8.75\times10^{-5}$ emu/(mol Cu). The nonsuperconducting sample shows a small Curie-like upturn below ~50 K. It is still unclear whether this upturn is intrinsic or not, because the estimated Cu^{2+} spin density for explaining this upturn is as small as 0.3% of all Cu atoms. In any case, because the Curie term is so small, the entire tendency above 100 K is not affected so much. It is noted that the susceptibility is increased with hole doping, whereas a slight negative temperature dependence is observed for both samples. These features are similar to those for $Tl_2Ba_2CuO_{6+\delta}$.[8] No significant changes are observed between the superconducting and metallic samples. It is interesting that the magnitude of the susceptibility per Cu [$\sim2\times10^{-4}$ emu/(mol Cu)] also agrees with those for $Tl_2Ba_2CuO_{6+\delta}$.[8]

V. CONCLUSION

We have observed a superconductor-to-metal transition due to overdoping through oxygen nonstoichiometry for $TlSr_2CaCu_2O_{7-\delta}$ having a Cu-O pyramidal layer. This ensures the general concept that the superconductivity is suppressed by too many carriers. The entire behavior of the transport and magnetic properties is quite similar to those for $Tl_2Ba_2CuO_{6+\delta}$, having a Cu-O octahedral layer. It is interesting that these two Tl compounds show great similarity in their physical properties in spite of the apparent difference in crystal structure. In particular, it is especially noted that no singularities of physical properties are observed at the superconductor-metal phase boundary for both compounds. We believe that this is indeed the intrinsic property of high-T_c cuprates in the overdoped region, although it is in contrast to the result for overdoped $La_{2-x}Sr_xCuO_4$.[2,18] An important difference between the Tl compounds and $La_{2-x}Sr_xCuO_4$ is that the Cu-O octahedron layer of the latter is fairly disordered by the Sr- substitution for La. For the Tl compounds, however, Cu-O octahedron or pyramid layers are essentially ordered because the oxygen nonstoichiometry occurs at the Tl layers separated enough from the Cu layer. Thus these Tl compounds are the best materials to investigate the properties in the overdoped region. The present results mean that HTSC is continuously connected to a normal metal with increasing carrier concentration. This implies that both HTSC and normal-metal states should be described on the same basis. However, it is also noted that the "normal-metal state" still shows anomalous behavior such as the temperature dependence of the Hall coefficient, which is not described as a simple Fermi liquid.

ACKNOWLEDGMENTS

We would like to thank F. Izumi and H. Asano for the neutron-diffraction study.

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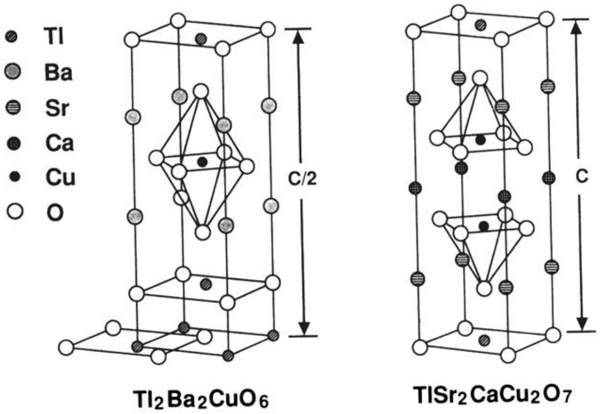

FIG. 1. Crystal-structure models for $Tl_2Ba_2CuO_6$ and $TlSr_2CaCu_2O_7$.