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Superconductivity in the Tl-Sr-Ca-Cu-O system

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Superconductivity at 20 K has been unambiguously observed in the Tl-Sr-Ca-Cu-O system. Superconductivity at 70 K was also observed in the same system. These observations may provide a new insight into the mechanism of oxide superconductivity.

Discoveries of Tl-based superconducting systems[1-5] and Bi-based superconducting systems[6-8] have not only set new T_c records with zero resistance up to 125 K, but also have provided a new insight into the mechanism of high-T_c oxide superconductivity. Compositional analyses and structure determinations of the new generation of rare-earth-free superconductors[9-15] have showed that (a) there are no Cu-O chains, but Cu-O sheets are apparently responsible for superconductivity in these new systems, and thus Cu-O chains which were thought important in rare-earth-based 1:2:3 compounds are not required for cuprate superconductivity; (b) T_c increases with the number of Cu-O layers per unit cell, the $Tl_2Ba_2Ca_2Cu_3O_{10+x}$ having the highest T_c (zero resistance at 125 K) has three Cu-O layers; and (c) buckling of Cu-O sheets of superconducting compounds may lead to decrease of T_c (Refs. 12 and 14).

The existing experimental data also indicate that group-II*A* elements are required for oxide superconductivity, playing perhaps a subtle role. Until now, Ba has been required for the Tl-based cuprate superconductors, whereas Sr is required for the Bi-based cuprate superconductors. At present, theorists are not able to predict whether superconductive compounds can be formed with substitution of Sr for Ba in the Tl-based cuprate superconducting systems, or substitution of Ba for Sr in the Bi-based cuprate superconducting systems. In extensive elemental substitutions for the Tl-based superconducting systems, we have observed 20-K superconductivity and possible 70-K superconductivity in the Tl-Sr-Ca-Cu-O system.[16] The samples are stable and the results are reproducible. The discovery of the Tl-Sr-Ca-Cu-O superconducting system bridges the Tl-Ba-Ca-Cu-O and Bi-Sr-Ca-Cu-O superconductors, and should provide further clues to an understanding of the mechanism of high T_c oxide superconductivity.

A typical procedure of preparing Tl-Sr-Ca-Cu-O superconducting samples is the following. Appropriate amounts of Tl_2O_3 (99.999% pure), SrO (99.5% pure), CaO (99.95% pure), and CuO (certificate reagent) were mixed and ground completely to obtain a powder with certain nominal compositions (for example, $Tl_2Sr_2Ca_2Cu_3O_{10+x}$). The powder was pressed into a pellet with a diameter of 7 mm and a thickness of 1-2 mm. The pellet was then put into a tube furnace which had been heated to 900-950 °C, and was heated for 3-5 min in flowing oxygen, followed by furnace cooling or quenching. Since a small amount (< 1%) of barium entering into the Tl-Ca-Cu-O system could lead to observation of superconductivity above liquid-nitrogen temperature,[17] great care was paid in avoiding contamination with barium. Qualitative chemical analyses were performed for samples 1 and 2 (both with a nominal composition of $Tl_2Sr_2Ca_2Cu_3O_{10+x}$) using a JSM model 35 scanning electron microscope, operated at 20 kV and 0.01 μA beam current. The major elements in both samples were Tl, Sr, Ca, and Cu. Sample 1, in addition, contains a trace (< 2%) of Ag, perhaps from silver paste or from capsule contamination. Neither sample contains detectable barium ($\ll 1\%$).

Electronic behavior of the Tl-Sr-Ca-Cu-O samples is strongly dependent on both the starting composition and the preparation conditions. Above liquid-nitrogen temperature, three patterns of temperature dependence of resistance were observed: semiconductive, semiconductive-metallic, and metallic. Most nominal $Tl_2Sr_2Ca_2Cu_3O_{10+x}$ samples prepared using the above procedure showed a metalliclike temperature dependence of the resistance above liquid-nitrogen temperature. Two of these samples (1 and 2, which were prepared by heating at 900 °C for 3 min followed by furnace cooling to 700 °C and by heating at 950 °C for 3 min followed by quenching to room temperature, respectively) were investigated down to liquid-helium temperature by four-probe resistance, dc SQUID magnetization, and the field derivative of the microwave absorption, dH''/dH, at 9.2 GHz (Ref. 18). The same investigations were also carried out for an additional sample (3) with a nominal composition of $Tl_2SrCa_2Cu_3O_{9+x}$, which was prepared by heating at

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900 °C for 3 min followed by quenching to room temperature and then annealing at 720 °C for 8 h. All of these samples showed superconductivity at about 20 K and another superconductive phase at about 70 K. It is noteworthy that in our preparation of the superconducting Tl-Sr-Ca-Cu-O samples, we used a short high-temperature heating technique as was used for the Tl-Ba-Cu-O and Tl-Ba-Ca-Cu-O samples.[1-5] High temperature is required for the initiation of the formation reaction of the superconducting compound, and short-duration heating minimizes the decomposition and evaporation of T_2O_3.

In Fig. 1(a) we present resistance versus temperature for sample 1. The onset temperature is about 22 K and zero resistance is reached at 10 K. In Fig. 1(b) we present the field-cooled and zero-field-cooled dc susceptibility versus temperature. As can be seen is an onset of diamagnetism at about 25 K. The diamagnetic shielding at the lowest temperatures is weak and corresponds to a superconducting volume fraction of less than 1%. In Fig. 1(c) we present the microwave spectrometer signal versus temperature. We find that there is a weak but abrupt change in dX''/dH (expended scale), indicating the onset of superconductivity at about 70 K. This is followed by a large increase in signal at lower temperatures, indicating that an increasing fraction of the sample becomes superconducting at temperatures below 20 K. This is consistent with both the susceptibility data [Fig. 1(b)] and the observed drop in the resistance [Fig. 1(a)].

Figures 2(a), 2(b), and 2(c) show resistance, magnetization, and microwave absorption data, respectively, versus temperature for sample 3. The temperature dependence of resistance [Fig. 2(a)] exhibits a metalliclike behavior down to 4.2 K, but with a step centered at 60 K (with a 20 K width). A change in slope near 75 K was also observed. The dc susceptibility shown in Fig. 2(b) indicates an onset of diamagnetism at about 70 K. Below 10 K the fraction of the sample which participates in diamagnetic shielding is 0.3% with a Meissner fraction of about half of that. The microwave absorption data of Fig. 2(c) indicate an onset temperature (expended scale) of about 70 K. Sample 2 also had similar characteristic indications of the onset of superconductivity (data not shown): i.e., a step in the resistance at 77 K, an onset of diamagnetism at about 70 K, and an onset of the microwave signal at about 80 K.

We interpret the above data as indicating that there are at least two superconducting phases, one with onset temperature at about 70 K and the other about 20 K, in the Tl-Sr-Ca-Cu-O system. We believe the superconducting phases are Tl-Sr-Ca-Cu-O, because (1) Tl-Sr-Cu-O sam-

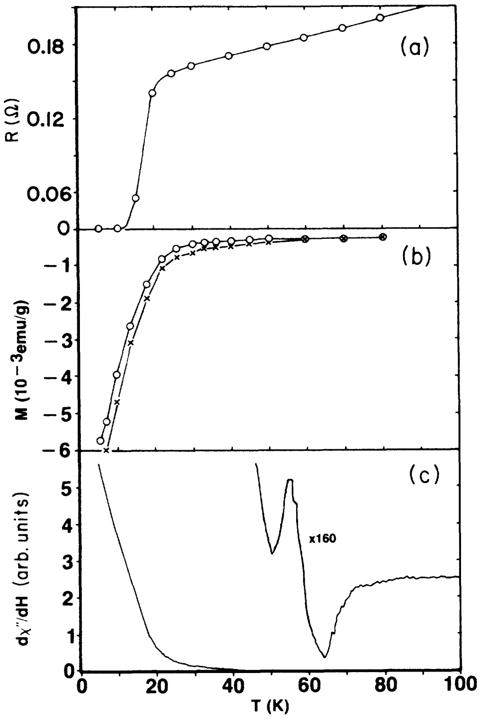

FIG. 1. (a) Resistance vs temperature for sample 1 (with a nominal composition of $Tl_2Sr_2Ca_2Cu_3O_{10+x}$. Zero resistance, which corresponds to resistivity $< 10^{-8}$ Ω cm, is reached at 10 K. The linear region extends up to 300 K. (b) Zero-field-cooled (cross points) and field-cooled (circle points) dc susceptibility vs temperature for an applied dc magnetic field of 100 G for sample 1. (c) Microwave spectrometer output (the field derivative of the absorption signal) vs temperature for an applied dc magnetic field of 40 G for sample 1.

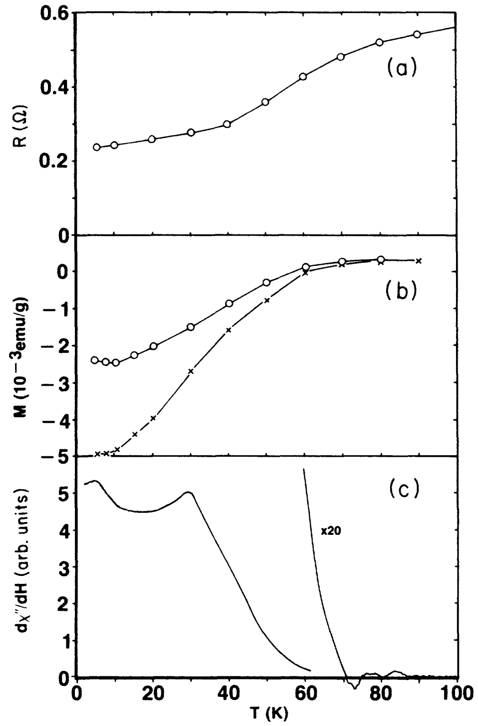

FIG. 2. (a) Resistance vs temperature for sample 3 (with a nominal composition of $Tl_2SrCa_2Cu_3O_{9+x}$). The linear region above about 80 K extends up to 300 K. (b) Zero-field-cooled (cross points) and field-cooled (circle points) dc susceptibility vs temperature for an applied dc magnetic field of 100 G for sample 3. (c) Microwave spectrometer output (the field derivative of the absorption signal) vs temperature for an applied dc magnetic field of 40 G for sample 3.

ples are not superconducting down to 4.2 K, although under similar preparation conditions they have metalliclike resistance-temperature behavior above liquid-nitrogen temperature, and although the Bi-Sr-Cu-O system is superconducting at about 20 K (Refs. 6 and 12); (2) the amount of Ba in the samples is not enough to account for the observed superconductivity; and (3) there is no other contamination sources which can cause the observed superconductivity. However, in all samples investigated down to 4.2 K, the Meissner and flux shielding signals are small, typically corresponding to less than 1% superconducting volume fraction. For this reason, we have not yet carried out chemical and structural identification of the superconducting phases, rather we are attempting to increase the portion of the superconducting phases, particularly that at about 70 K. Nevertheless, it may be surmised that if the Tl-Sr-Ca-Cu-O superconductors have structures similar to those of the corresponding Tl-Ba-Ca-Cu-O and Bi-Sr-Ca-Cu-O superconductors, their Cu-O sheets would be more buckled reflecting their lower T_c (Refs. 12 and 14), or alternatively, they may simply have their own alternative structures.

In summary, we have demonstrated that the Tl-Sr-Ca-Cu-O system has at least two superconducting phases, one with onset temperature at about 70 K, and the other about 20 K. At present the procedure of sample preparation limits the volume fraction of the superconducting phases to less than 1%, but further experiments focused on increasing this volume fraction, so as to allow ready chemical and structural analysis, are in progress.

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[16] We have received a copy of the unpublished work, by W. L. Lechter, M. S. Osofsky, R. J. Soulen, Jr., V. M. LeTourneau, E. F. Skelton, S. B. Qadri, W. T. Elam, H. A. Hein, L. Humphreys, C. Skowronek, A. K. Singh, J. V. Gilfrich, L. R. Toth, and S. A. Wolf, which reports 119- and 70-K superconductivity onset in the Tl-Sr-Cu-O system contaminated by 7% of Ca.

[17] Z. Z. Sheng and A. M. Hermann (unpublished).

[18] Many groups have reported measurements of dX''/dH at microwave frequencies [see session R8 in Bull. Am. Phys. Soc. **33**, 774 (1988) and S8 *ibid.*, **33**, 807 (1988); see also K. W. Blazey, A. M. Portis, K. A. Muller, and J. G. Bednorz, [Solid State Commun. (to be published)]; and S. H. Glarum, J. H. Marshall, and L. F. Schneemeyer, Phys. Rev. B **37**, 7491 (1988), and references therein.] We have made an extensive study of the utilization of these signals for the specific purpose of detecting the onset of superconductivity in samples which only contain a small volume fraction of a superconducting phase. The details of our tests will be presented elsewhere, but in brief, we find that under the appropriate spectrometer operating conditions the technique is both extremely sensitive (<1 μg) and reliable, (i.e., readily discriminates against other mechanisms contributing to a temperature dependence of the microwave absorption).