Magnetization of the 120-K Tl-Ca-Ba-Cu-O superconductor

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dc magnetization measurements on the new Tl-Ca-Ba-Cu-O superconductor show superconductivity with an onset temperature as high as 118 K, 24 K higher than that of a high-quality $EuBa_2Cu_3O_{7-x}$ sample. The resistive onsets of these new superconductors are near 140 K. The magnetic data show complete diamagnetic flux exclusion and 10–15% Meissner expulsion at 10 K.

Discoveries of 30-K superconductivity in the La-Ba-Cu-O system[1] and 90-K superconductivity in the Y-Ba-Cu-O system[2] have stimulated a worldwide race for higher-temperature superconductors. In spite of many efforts in the past year, stable and reproducible superconductivity has remained at the level of 90 K in the *R*-Ba-Cu-O system (*R* equals rare earth). Breakthroughs were recently made in rare-earth-free superconductors by the discoveries of the 90-K Tl-Ba-Cu-O system,[3,4] 110-K Bi-Ca-Sr-Cu-O system,[5,6] and 120-K Tl-Ca-Ba-Cu-O system.[7-9] The Tl-Ca-Ba-Cu-O superconducting samples have onset and zero-resistance temperatures much higher than those of the Bi-Ca-Sr-Cu-O system.[7-9] Two superconducting phases have been identified.[9] One has a composition of $Tl_2Ca_2Ba_2Cu_3O_{10+x}$ (2:2:2:3 phase), and another of $Tl_2CaBa_2Cu_2O_{8+x}$ (2:1:2:2 phase, which is similar to $Bi_2CaSr_2Cu_2O_{8+x}$). In this Brief Report we report magnetization and resistance data on the Tl-Ca-Ba-Cu-O samples. The onset temperature of magnetization is 117–118 K, 23 K higher than that of a high-quality $EuBa_2Cu_3O_{7-x}$ sample.

Two samples with nominal compositions $Tl_2Ca_2BaCu_3O_{9+x}$ and $Tl_2Ca_4BaCu_3O_{11+x}$ used in the present experiments were prepared using Tl_2O_3, CaO, and $BaCu_3O_4$ in the same batch.[8] Both were heated at 900 °C for 3 min and furnace cooled. The resistance-temperature dependences of these two samples are shown in Fig. 1. The resistance was measured by the standard four-probe technique with silver-paste contacts. These two samples both have onset temperatures near 140 K (defined by the smallest curvature of the resistance-temperature curve[10]), midpoint of 127 K, and zero-resistance temperature at 121 K. Zero-resistance data correspond to resistivities less than 10^{-6} Ω cm. The difference of calcium contents in these two samples does not seem to have significantly changed their superconducting behavior, which depends strongly on preparation conditions of the samples. Note that the $Tl_2Ca_2BaCu_3O_{9+x}$ sample consists of approximately 80% of the new 2:2:2:3 superconducting phase.[9]

Magnetization measurements were performed utilizing a superconducting quantum interference device (SQUID) magnetometer manufactured by BTI Corp., San Diego, CA. Figures 2 and 3 show dc magnetization (field cooled and zero field cooled) as a function of temperature for an applied field of 1 mT for samples of $Tl_2Ca_2BaCu_3O_{9+x}$ and $Tl_2Ca_4BaCu_3O_{11+x}$, respectively, whose resistive behavior is shown in Fig. 1. The Meissner flux expulsion is 10–15% of the diamagnetic flux exclusion; the magnitude of the diamagnetic shielding is large and consistent with complete flux exclusion from the samples at 10 K. This behavior is similar to that observed in Tl-Ba-Cu-O,[4] La-Ba(Sr)-Cu-O,[11] and Y-Ba-Cu-O samples.[12] Explanations suggested to date include existence of a superconducting glass state,[11] anisotropy effects,[13] and superconductivity confined to thick shells around normal grains.[12] At this stage, we hesitate to speculate on differentiation between these causes, and only note that our samples were

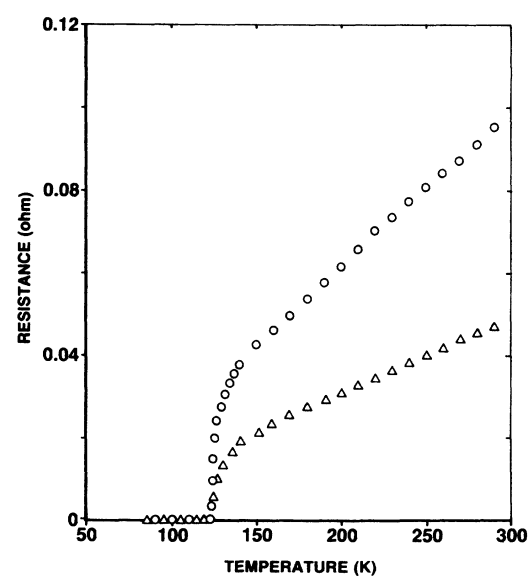

FIG. 1. Resistance-temperature dependences of samples $Tl_2Ca_2BaCu_3O_{9+x}$ (triangles) and $Tl_2Ca_4BaCu_3O_{11+x}$ (circles).

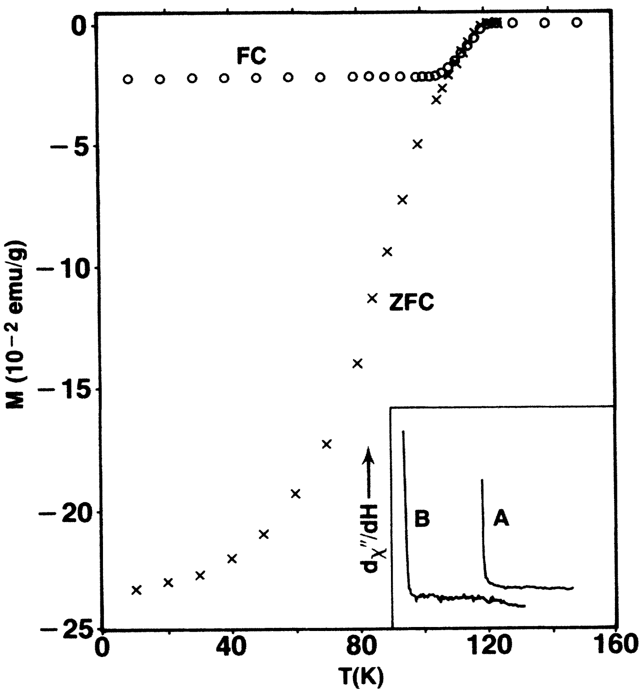

FIG. 2. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization as a function of temperature for a dc field of 1 mT for a sample of $Tl_2Ca_2BaCu_3O_{9+x}$. The two data traces in the inset illustrate the sharp onset of superconductivity observed by the microwave technique as described in the text. Sample *A* is $Tl_2Ca_2BaCu_3O_{9+x}$ with onset temperature of 117.2 K, and for comparison, data for a sample of $EuBa_2Cu_3O_{7-x}$ (sample *B*) with onset temperature of 94.4 K is plotted. Note that the difference in onset is 22.8 K.

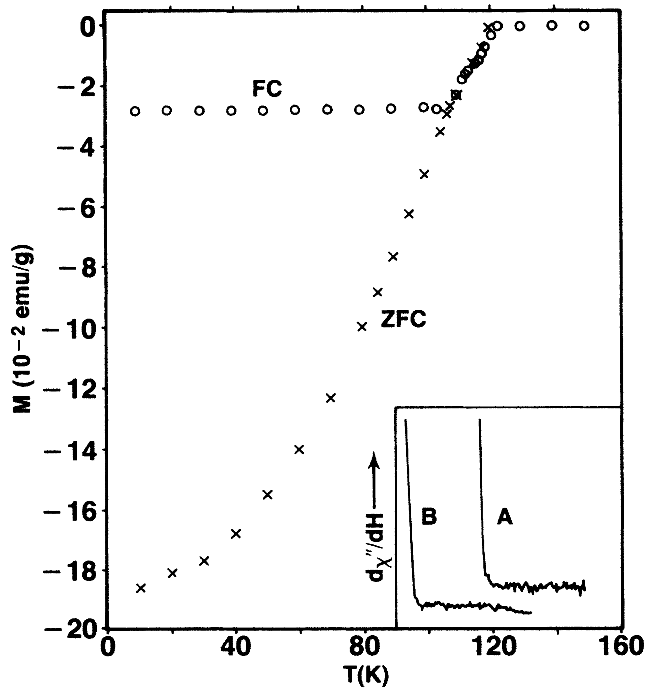

FIG. 3. Field-cooled (FC) and zero-field-cooled (ZFC) magnetization as a function of temperature for a dc field of 1 mT for a sample of $Tl_2Ca_4BaCu_3O_{11+x}$. The two data traces in the inset illustrate the sharp onset of superconductivity observed by the microwave technique as described in the text. Sample *A* is $Tl_2Ca_4BaCu_3O_{11+x}$ with onset temperature of 118.3 K, and for comparison, data for a sample of $EuBa_2Cu_3O_{7-x}$ (sample *B*) with onset temperature of 94.4 K is plotted. Note that the difference in onset temperatures is 23.9 K.

prepared by a short-duration heating technique.

In the insets of Figs. 2 and 3, we present data traces for these two samples, and also for a well-prepared $EuBa_2Cu_3O_{7-x}$ sample, where the vertical axis represents the $d\chi''/dH$ signal of an EPR spectrometer. The full details of how we apply this technique will be presented elsewhere, but in brief, we have examined diverse high-T_c samples including ceramic, powder, single-crystal, and epitaxial films, and find that for properly optimized conditions the temperature dependence of the spectrometer output may be taken as a sensitive indication for the onset of superconductivity. As is seen from the inset of Fig. 2, the onset temperature for the sample *A* ($Tl_2Ca_2BaCu_3O_{9+x}$) is 117.2 K, and, for comparison, for sample *B* ($EuBa_2Cu_3O_{7-x}$), the corresponding value is 94.4 K (the difference in onset temperature between the Tl-Ca-Ba-Cu-O sample and the Eu-Ba-Cu-O sample is 22.8 K). Similarly, from the inset of Fig. 3, the corresponding value for the sample $Tl_2Ca_4BaCu_3O_{11+x}$ is 118.3 K, 23.9 K higher than that of the Eu-based sample. These onset temperatures are consistent with those measured by resistance-temperature variations.

In conclusion, the Tl-Ca-Ba-Cu-O samples show a complete diamagnetic exclusion, and 10–15% Meissner expulsion at 10 K. The onset temperature of magnetization drop for the Tl-Ca-Ba-Cu-O samples is 118 K, which is 23.5 K higher than that for a high-quality $EuBa_2Cu_3O_{7-x}$ sample. This onset temperature is consistent with that observed from resistance-temperature variations.

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