Thermoelectric power of the Tl-Ca-Ba-Cu-O superconductor

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We report measurements of the thermoelectric power of the high-temperature Tl-Ca-Ba-Cu-O superconductor. The data indicate a transition which is centered at 118 ± 3 K, in agreement with magnetic measurements and published resistivity results. The thermoelectric power is positive and, aside from the high transition temperature, is remarkably similar in magnitude and temperature dependence to that of the rare-earth-based oxide superconductors which have been reported previously.

Since the discovery of high-temperature oxide superconductors in 1986 by Bednorz and Müller,[1] at least three families of such materials have been identified. The first group, containing La-Ba-Cu-O and its derivatives, exhibits superconductivity in the range of 30–40 K. The second group, discovered by Chu and co-workers,[2] is described by R-Ba-Cu-O, where R represents one of the rare-earth elements or yttrium. These materials exhibit transitions in the 90-K range. Recently, a new family has been discovered with even higher transition temperatures in the range of 115–120 K. Remarkably, the new materials do not contain yttrium or any of the rare-earth elements. One type, which has been studied by several workers,[3–5] contains the element bismuth. A second type, first announced by Sheng and Hermann,[6] and later confirmed by others,[7] is distinguished by the presence of thallium. The purpose of this note is to describe recent measurements of the thermoelectric power of this new material.

The samples were prepared at the University of Arkansas from $Ba_2Cu_3O_5$ and oxides of thallium and calcium. The powders were mixed, ground, pressed into pellets, and then heated to about 900 °C in flowing oxygen for 3 min. The sample was furnace cooled by turning off the furnace for 1 h and then removed. These procedures have been described in more detail in previous publications.[6,8]

The apparatus and procedures for the thermoelectric power measurements have also been described in an earlier paper.[9] A differential method was employed in which a voltage difference is measured across the sample in response to an imposed temperature difference. Two sets of reference leads (Constantan and Chromel) were used and the voltages, after correcting for the thermoelectric power of the leads, were averaged to obtain the final results. The measurements were made in vacuum as the sample slowly warmed from liquid-nitrogen temperature to ambient.

Figure 1(a) shows the thermoelectric power data for a sample with nominal composition $Tl_{2.2}Ca_2Ba_2Cu_3O_{10.3+x}$.

Energy-dispersive x-ray measurements on this sample indicated a composition of $Tl_{2.20}Ca_{2.00}Ba_{2.14}Cu_{3.72}O_y$. Figure 1(b) shows thermoelectric power data for a Y-Ba-Cu-O sample for comparison. In either case the normal-state thermoelectric power is positive, indicating dominant hole conduction, and drops rapidly to zero at the superconductive transition. The apparent transition for both samples is somewhat broadened by the temperature difference of several degrees which was imposed during the measurements. The midpoint of the transition was determined to lie at 118 ± 3 K. This is in good agreement with data taken at 1 MHz by a magnetic induction technique[10] which showed an onset of screening at about 115 K. The midpoint of the thermoelectric transition for the Y-Ba-Cu-O sample is 93 ± 2 K.

Resistance was measured by the standard four-probe technique using silver-paste contacts. Figure 2 shows the temperature dependence of the resistance for a piece of the sample of Fig. 1(a). From this curve it is seen that the onset of the resistive transition is about 120 K, the midpoint is 110 K, and the sample reaches zero resistance (less than 10^{-6} Ω cm) at 104 K.

At least three separate ranges of temperature-dependent behavior are apparent in the thermoelectric power data of Fig. 1. Below the transition, this quantity is required to vanish on thermodynamic grounds. From the transition temperature to about 175 K in both samples, the thermoelectric power is an increasing function of temperature. Finally, from 175 K to room temperature, we observe a linear decrease with increasing temperature. The pronounced peak near 175 K in the data for both samples is believed to be intrinsic. Careful calibration of the thermoelectric power of the reference leads, as well as measurements on nonsuperconductive materials in this temperature range, have revealed no other explanation for this feature.

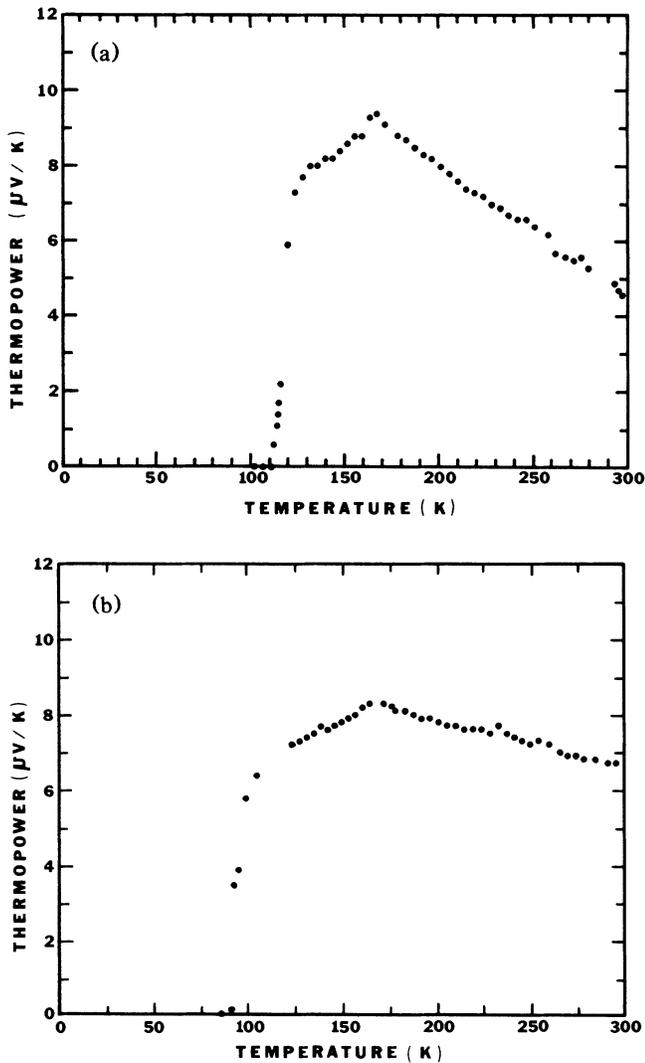Several reports on the thermoelectric powers of oxide superconductors have appeared in the literature.[11–17] In

FIG. 1. (a) Thermoelectric power of $Tl_{2.2}Ca_2Ba_2Cu_3O_{10.3+x}$ (nominal stoichiometry) as a function of temperature. The experimental uncertainty is ± 1 V/K. (b) Thermoelectric power of Y-Ba-Cu-O (from Ref. 9).

FIG. 2. Temperature dependence of the resistance of $Tl_{2.2}Ca_2Ba_2Cu_3O_{10.3+x}$.

the transport of carriers in a narrow-band Hubbard model with site-correlation energy U. In the limit of $U \gg k_B T$, the proposed thermopower is[19]

$$S = (k_B/e)\ln[x/2(1-x)] , \tag{1}$$

where x is the fractional occupancy of the band. This formula yields positive thermoelectric powers for $x > \frac{2}{3}$, and magnitudes in agreement with reported data for reasonable values of x. Furthermore, the extreme sensitivity of the thermoelectric power to oxygen content, such as has been reported for Eu-Ba-Cu-O,[20] may have a natural ex-

particular, Mawdsley et al.[13] have observed behavior similar to that of Fig. 1(b) in experiments on the Y-Ba-Cu-O system. They attribute the intermediate range with positive temperature coefficient to diffusive thermopower of holes within the grains of the superconductive material, enhanced by electron-phonon interactions. They ascribe the decrease at high temperatures to a competing semiconducting path through n-type inclusions. The range of increasing thermopower is then determined by the quality and homogeneity of the sample. In this context, scanning electron microscopy observations indicate that the present material is much less crystalline than the Y-Ba-Cu-O compound and has more platelike, layered structures as shown in Fig. 3.

A useful model has recently been proposed by Fisher et al.[18] to explain the high-temperature thermoelectric power of Y-Ba-Cu-O as a function of changing oxygen content, especially above 700 °C. These authors consider
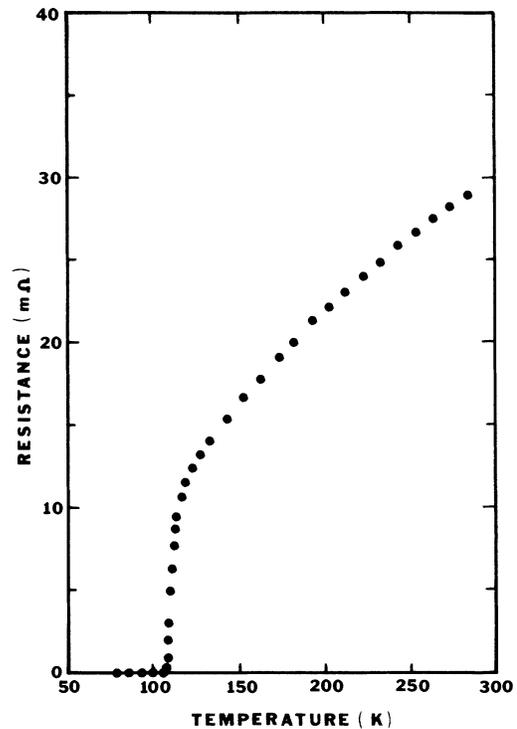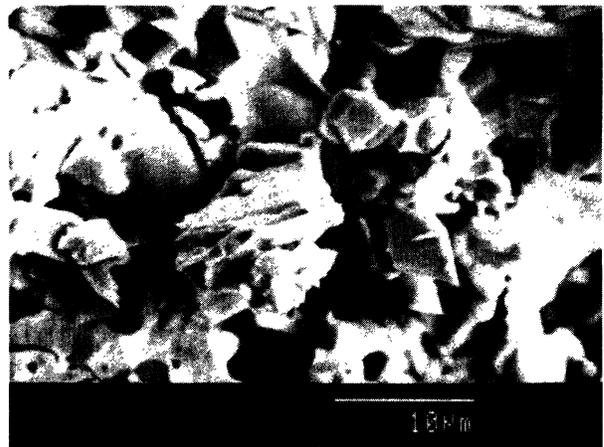

FIG. 3. Electron micrograph showing scale and layered structures of $Tl_{2.2}Ca_2Ba_2Cu_3O_{10.3+x}$ specimen.

planation in terms of this model. Within this framework, the observed maximum of 10 $\mu V/K$ in the Tl-Ca-Ba-Cu-O data implies a narrow band with fractional occupancy of about 0.7 according to Eq. (1). The temperature dependence of the data is currently under study within the framework of this model, including contributions from inclusions.

The similarity of the data for Tl-Ca-Ba-Cu-O and Y-Ba-Cu-O shows clearly that the transport mechanisms in the normal state, and likely the mechanisms of superconductivity as well, are closely related in the two families of materials. Further studies of compounds formed by the substitution of new elements, and modifications of their oxygen contents, should lead to a clarification of the dominant transport mechanisms and contribute to the explanation of superconductivity in these systems.

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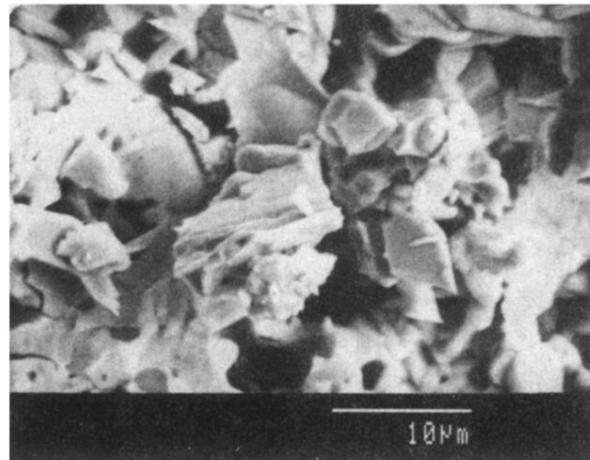[20]R. S. Kwok, S. E. Brown, J. D. Thompson, Z. Fisk, and G. Gruner (unpublished).

FIG. 3. Electron micrograph showing scale and layered structures of $Tl_{2.2}Ca_2Ba_2Cu_3O_{10.3+x}$ specimen.