Superconductivity at 90 K in a multiphase oxide of Y-Ba-Cu

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We have measured the resistance and dc susceptibility in a series of multiphase Y-M-Cu oxides, where M = Ca, Sr, and Ba. We find superconductivity in two of the Ba samples, of nominal composition $Y_{2-x}Ba_xCuO_{4-y}$ with x = 0.20 and x = 0.25. For x = 0.25, the midpoint of the resistive transition is 91 K, the resistance has reached zero by 83 K, and the Meissner signal reaches 2% of that expected for an ideal bulk superconductor at low temperatures.

The recent discovery[1] of superconductivity in the oxides La-Ba-Cu-O has generated an intense search for superconductivity in related materials. Bulk superconductivity was confirmed in the $La_{2-x}M_xCuO_{4-y}$ system,[2,3] with M = Ba, Sr, Ca, and x between 0.1 and 0.3, and critical temperatures (T_c) as high as 40 K have been reported in single-phase compounds.[4] Even higher values of T_c have been reported in multiphase materials[5] or in materials under pressure.[6]

Even more recently superconductivity above 90 K has been reported,[7] possibly in the Y-Ba-Cu-O system.[8] We have prepared a series of multiphase oxides of Y, Cu, and M, where M = Ca, Ba, Sr, and find a superconducting transition for M = Ba at 91 K, as determined by the midpoint of the transition in the resistivity, and a Meissner signal of about 2% of the ideal value. Our samples have at least three phases, and the superconducting phase has not been identified.

Samples of average composition $Y_{2-x}M_xCuO_{4-y}$ (x = 0.15, 0.2, 0.25, and M = Ca, Sr, Ba) were prepared from appropriate amounts of Y_2O_3, CuO, and MCO_3, all 99.999% pure. The materials were mixed, and pressed into a pellet of 12 mm diameter at 10 kbar. They were then heated in a platinum boat in a tubular furnace under flowing oxygen to 1100 °C in 12 h, held at the temperature for 48 h, and cooled to room temperature in 3 h. The Sr samples are black, the Ba samples black with a green hue, and the Ca samples black with flecks of white. Rectangular bars $12 \times 3 \times 0.7$ mm were cut from the pellets for resistance measurements, and pieces of the pellets were ground for magnetic measurements and powder x-ray diffraction. The samples used in this study are over one month old, indicating that the superconducting phase is stable at least for this long.

Resistivities were measured using a standard four-probe method on samples with silver-paint contacts. Current densities ranged from 5 $\mu A/cm^2$ to 5 mA/cm^2. The dc magnetic susceptibility was measured with a superconducting quantum interference device magnetometer on samples cooled in a field (Meissner effect) and warmed in a field after cooling in zero field (shielding effect). The thermometers used in both resistivity and susceptibility measurements were calibrated to ± 0.2 K. The samples were characterized by powder x-ray diffraction in the Bragg-Brentano geometry with Cu $K\alpha$ radiation.

X-ray diffraction shows that all the samples contain at least three phases. The dominant phases in each sample are Y_2O_3 and $Y_2Cu_2O_5$. The other phases have not been identified. For a given M, the fraction of $Y_2Cu_2O_5$ phase decreases as x increases from 0.15 to 0.25. Moreover, for each M there is a third phase which does not change noticeably with x. The diffraction peaks of this phase are given in Table I for M = Ba. Several compounds also have a fourth phase that is unique for a particular M and x. The lines unique to M = Ba and x = 0.25 are also given in Table I. Figure 1 shows the diffraction pattern for M = Ba and x = 0.25, indicating the two unidentified phases. We do not know which of these phases, if either, is responsible for the superconductivity, or even if these "phases" are actually several phases. A sample M = Ba, x = 0.25 was arc melted, and the resulting compound was no longer superconducting. The arc-melted sample was black (brown after powdering), rather than green, and according to x-ray diffraction was mainly Y_2O_3. The peaks of $Y_2Cu_2O_5$ had disappeared, but some new (unidentified) peaks had appeared.

Of the nine compositions studied, only those with M = Ba and x = 0.20 and 0.25 show superconductivity, as

TABLE I. Unidentified diffraction peaks for $Y_{2-x}Ba_xCuO_{4-y}$, x = 0.25. Values of d are distances between adjacent atomic planes. The intensities are normalized to the height of the strongest peak in the diffraction pattern, at 29° in Fig. 1. The peaks in (a) are also observed for x = 0.20 and 0.15; those in (b) are not observed for x = 0.20 and 0.15.

2θ (deg)	(a) d (Å)	Intensity
29.86	2.990	15
31.64	2.826	6
31.98	2.796	3
38.79	2.320	3
40.76	2.212	5
45.62	1.987	6
2θ (deg)	(b) d (Å)	Intensity
32.60	2.745	5
32.89	2.721	6
35.62	2.518	5
48.79	1.865	6

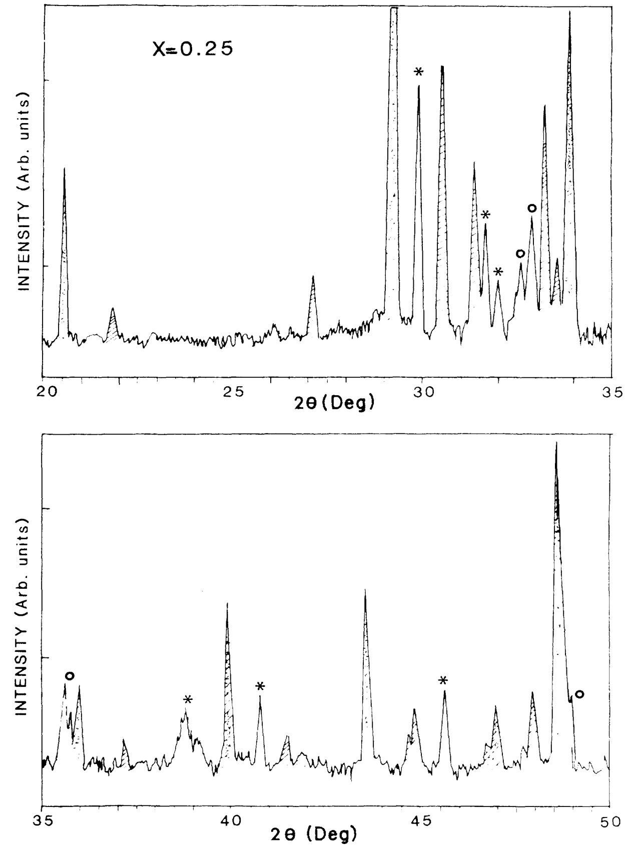

FIG. 1. Powder x-ray diffraction pattern for Cu $K\alpha$ radiation. The peaks are labeled as follows: shaded by dots, Y_2O_3; shaded by lines, $Y_2Cu_2O_5$; asterisk, the peaks seen in all M = Ba samples; and open circle, the peaks seen only for $x=0.25$. The positions of the unidentified peaks are given in Table I.

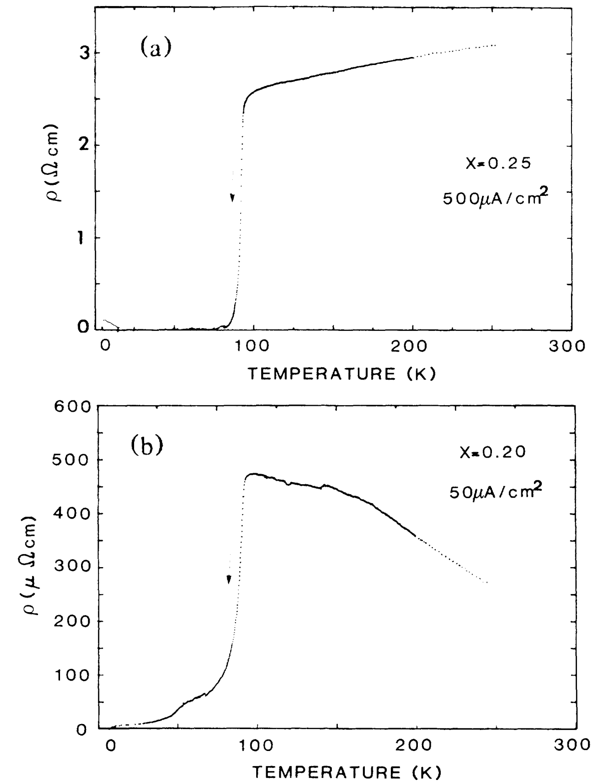

FIG. 2. Resistance vs temperature for M = Ba in $Y_{2-x}M_x$-CuO_{4-y}. (a) $x=0.25$, current density 500 $\mu A/cm^2$; (b) $x=0.20$, current density 50 $\mu A/cm^2$.

measured with magnetic susceptibility. Figure 2 shows the resistivity for those samples. The resistivity at room temperature ρ(300 K) is about 3 Ω cm for $x=0.25$, 200 $\mu\Omega$ cm for $x=0.20$, and greater than $10^6 \Omega$ cm for $x=0.15$. This strong, nonmonotonic dependence of ρ(300 K) on x is probably caused by changes in the relative amounts of the various phases, and indicates the presence of a minority metallic component only near the compositions $x=0.2$ and $x=0.25$. The small decrease in resistivity in Fig. 2(b) at 140 K is reproducible on different temperature sweeps, and moves to lower temperature at higher currents; we are still studying it.

Figure 3 shows the transitions in more detail. For $x=0.25$ at 100 $\mu A/cm^2$, the transition is complete at 82 K. We saw appreciable hysteresis in the transition at cooling rates of about 100 K/h, may be due to poor thermal contact between our sample and thermometer; on heating, the midpoint of the transition is 90 K and on cooling 92 K, and the width from 10 to 90% of the resistive transition is 4.5 K. For $x=0.20$ at 50 $\mu A/cm^2$, the transition is complete only at about 10 K, the midpoint is 91.5 K on cooling and 87.5 K on heating, and the transition is 30 K wide from 10% to 90% resistive signal. At 100 $\mu A/cm^2$ in the sample $x=0.2$, the resistance drops by about a factor of 10 between 100 and 10 K, but does not disappear by this temperature.

Critical-current measurements indicate that the superconducting phase is filamentary. Measurements of voltage versus current for $x=0.25$ at 77 K show that the voltage across the sample first exceeds our resolution of 0.1 μV between current densities of 5 and 15 mA/cm^2 on different current sweeps, and then smoothly increases, reaching half the voltage expected in the normal phase at current densities that varied from 20 to 35 mA/cm^2. The smooth increase and the irreproducibility are both arguments for a filamentary superconducting phase. At 5 K for $x=0.25$ the critical current exceeds 7.5 A/cm^2. On occasion, however, we have seen indications of nonzero resistance below 10 K for $x=0.25$, as well as anomalies in the magnetic properties, which we are still studying.

The magnetic measurements in Fig. 4 confirm that only a fraction of the sample is superconducting. The samples were powders, lightly packed in a tube 3 mm in internal diameter and 4 mm long. Estimating 50% porosity in the powders, the Meissner signal for M = Ba is 2% and 0.6% of that expected for bulk superconductivity for $x=0.25$ and $x=0.2$, respectively. The transitions are broader in the Meissner and shielding measurements than in the resistance, as in $La_{2-x}M_xCuO_{4-y}$.[4] The 2% Meissner signal for $x=0.25$ suggests that the superconducting phase, if crystalline, might be seen by x-ray powder diffraction and so could be one of the two unidentified

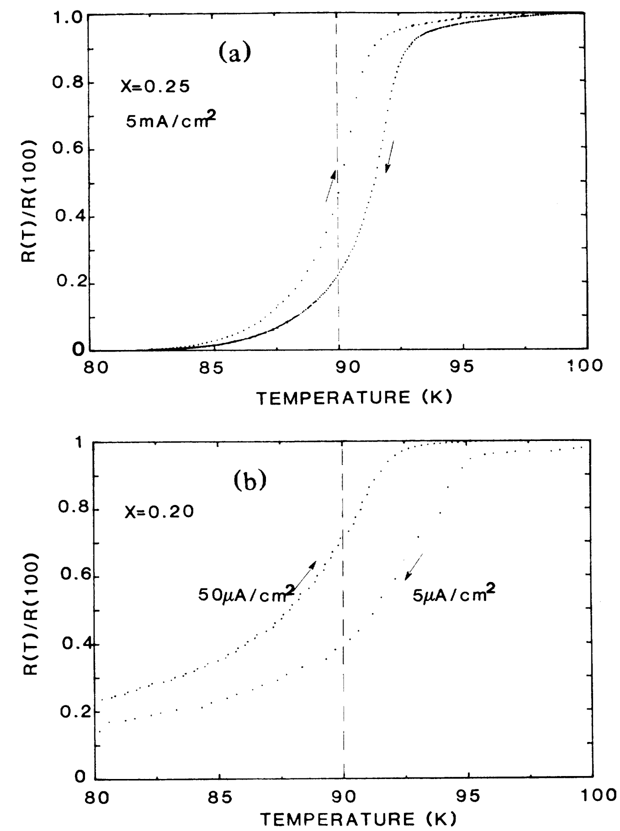

FIG. 3. Resistance vs temperature for $M = \mathrm{Ba}$ in $Y_{2-x}M_xCuO_{4-y}$, for increasing and decreasing temperature, as indicated by the arrows. (a) $x = 0.25$, current density 5 mA/cm^2; (b) $x = 0.20$, current density 50 $\mu A/cm^2$ for increasing temperature, and 5 $\mu A/cm^2$ for decreasing temperature.

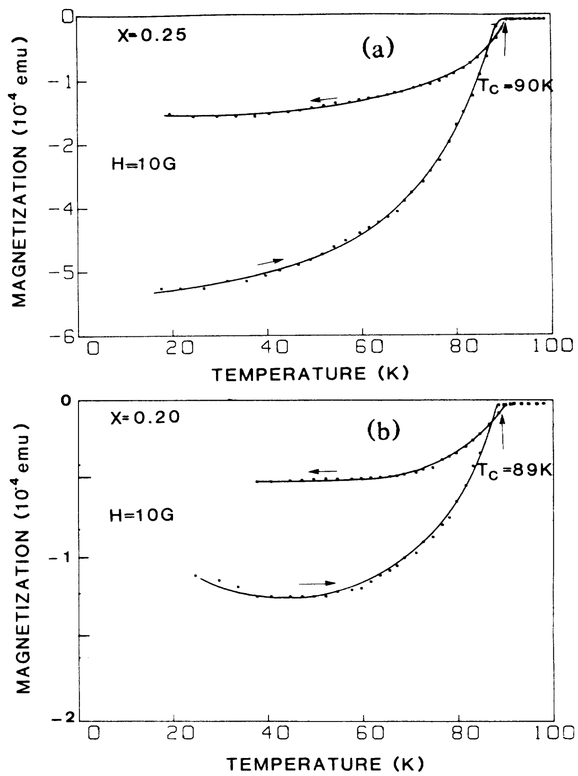

FIG. 4. Magnetic moment (in emu) vs temperature for $M = \mathrm{Ba}$ and (a) $x = 0.2$ and (b) $x = 0.25$ in $Y_{2-x}M_xCuO_{4-y}$, in a magnetic field of 10 G. As indicated by the arrows, the upper curves are for cooling in a field (Meissner effect) and the lower curves are for heating in a field after cooling in zero field (shielding effect). The samples were powders, 0.095 g and 0.098 g for $x = 0.25$ and $x = 0.2$, respectively, in a cylinder 3 mm in diameter and 4 mm long. Based on the volume and a packing fraction of 50% (or on the mass and a density of 7 g/cm^3), the Meissner signal at 10 K is 2% and 0.6% of that for a perfect diamagnet for $x = 0.25$ and $x = 0.2$, respectively.

phases in Table I and Fig. 1. The superconducting signal cannot be measured at high fields, because of a strong paramagnetic signal from the other phases.

In summary, the size of the Meissner signal and the zero resistance suggests the existence of bulk superconductivity in one of the phases in these multiphase Y-Ba-Cu oxides. On the other hand, the width of the transition in the Meissner signal suggests inhomogeneities in the superconducting phase. The rapid increase in the highest known T_c in recent months encourages speculation that even higher T_c's will be found, and clearly many people will investigate small changes in resistance, such as that in Fig. 2, in these multiphase systems.

Note added in proof. We have since isolated the superconducting phase as $YBa_2Cu_3O_{8-x}$ and determined the single crystal structure [LePage *et al.*, this issue, Phys. Rev. B **35**, 7245 (1987)].

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