Superconductivity in the Y-Sr-Cu-O system

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Samples with the nominal composition $YSrCuO_{4-y}$ processed at temperatures above 1200 °C exhibit two superconducting transitions, one at 80 K and another at 40 K. The 80-K transition may be due to the 1:2:3 phase, and the 40-K transition to the 2:1:4 phase. The dc magnetic-moment measurements showed an anomaly at 14 K, which suggests the possible existence of a magnetically ordered state.

During our early work on the new cuprate superconductors, we found that there seemed to be a correlation between the T_c and the ionic sizes of the metallic elements involved. Guided by this observation and the assumption that an optimal interatomic distance might exist in the K_2NiF_4 structure for a high-T_c compound, we successfully fabricated the first 90-K multiphase Y-Ba-Cu-O superconductor.[1] The T_c remains in the 90-K range in analogous rare-earth 1:2:3 compounds[2] in which the Y^{3+} ions are replaced by stable trivalent rare-earth ions with radii comparable to that of the Y^{3+} ion. The substitution of the copper ions by transition-metal ions,[3] however, generally results in the lowering of T_c or the disappearance of superconductivity. Complete replacement of the Ba^{2+} ions with the smaller alkaline earth metal ions (Sr^{2+}, Ca^{2+}, or Mg^{2+}) has not produced high-T_c superconductors. Thus far, only $Y_{0.3}Sr_{0.7}CuO_{3-y}$ with a T_c of about 40 K has been reported.[4]

In the process of making the first 90-K superconductors, we observed that samples reacted at temperatures higher than 950 °C for comparatively short firing times exhibited sharper transitions. Recently, using high-temperature processing, we have successfully converted the semiconducting 2:1:1 phase (Y_2BaCuO_5) to the superconducting 1:2:3 phase ($YBa_2Cu_3O_7$), and synthesized a new cuprate oxide superconductor involving only non-rare-earth elements, $BiSrCuO_y$.[5] We have also used high temperatures to process yttrium-strontium-copper-oxide samples. In this Brief Report, we report the observation of high-T_c superconductivity at 80 K and an anomalous magnetic moment at 14 K in the Y-Sr-Cu-O system.

A sample with a nominal composition $YSrCuO_{4-y}$ was prepared by mixing appropriate amounts of Y_2O_3, SrO, and CuO. The mixture was ground and pressed into pellets, heated to 1300 °C for 2 h, and then quenched to room temperature (RT). The material was then reground, pressed, and reheated to 1200 °C for 6 h in O_2, and then slowly cooled to RT. High-purity alumina crucibles were used in the sample preparation. Samples were cut into $1\times1\times3$ mm^3 bars for resistivity and magnetic-moment measurements. Electrical resistivity was measured using a conventional four-probe technique. The magnetic-moment measurements were made with a superconducting quantum interference device (SQUID) magnetometer at the National Magnetic Laboratory at MIT. A standard four-probe method using pulse currents was used to determine the critical current density at zero field. Structural and phase determinations were provided by x-ray diffraction (XRD) and Raman microprobe analysis.

The electrical resistance R of the sample as a function of temperature is shown in Fig. 1. The current used was 1 mA. The superconductivity transition was sharp with an onset at 92 K and zero resistance at 85 K. A linear temperature dependence of R before the onset of superconductivity was observed. This behavior is similar to that of $YBa_2Cu_3O_7$,[1] except that the initial R was about two orders of magnitude larger. The I-V curve of the sample at 4.2 K exhibits characteristics of a superconductor [Fig. 1 (inset)]. The critical current density was estimated to be 145 A/cm^2. This relatively low current density suggests that the sample is not single phase. The presence of several phases is confirmed by XRD results listed in Table I.

Although the resistance curve of our sample does not indicate the presence of a second superconductivity transition, the I-V curve clearly reveals the existence of two superconducting phases, indicated by the two different slopes in the curve. In addition, measurements of the dc magnetic moment (m) on a 25-mg sample also indicated a superconducting transition at 80 K, and another at 40 K (Fig. 2).

The XRD and Raman analyses were performed on the sample to learn more about the 80- and 40-K superconducting phases. The XRD pattern was complex and could

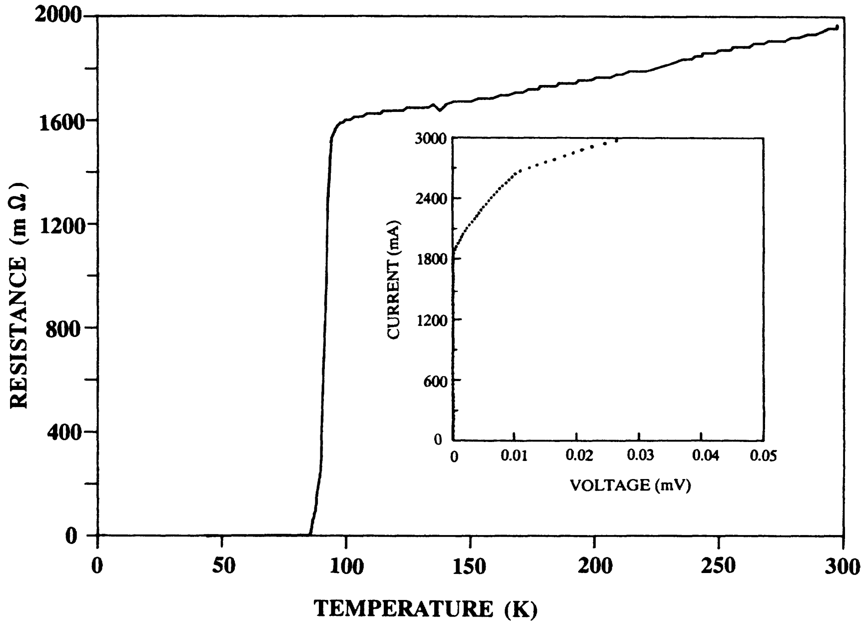

FIG. 1. The electrical resistance of a sample with a nominal composition $YSrCuO_{4-y}$. Inset: The *I-V* characteristic at 4.2 K.

not be exactly indexed to either the 1:2:3 phase or the 2:1:4 phase. However, the main peaks of the XRD pattern could be fitted fairly well if the Sr^{2+} ions were assumed to replace the Ba^{2+} ions in the 1:2:3 crystal structure.[6] The resulting lattice constants were $a=3.824$, $b=3.798$, and $c=11.435$. The 40-K superconducting phase may be attributed to an orthorhombic phase with lattice constants similar to those of the 2:1:4 phase. However, samples with a nominal composition $YSr_2Cu_3O_7$ failed to produce any superconducting phases, when processed under similar conditions. The Raman spectrum of the $YSrCuO_y$ sample in the 100–800 cm^{-1} region shows several peaks [Fig. 3(b)] which differ from those of the 1:2:3 phase [Fig. 3(a)] or the 2:1:4 phase. In addition, no Raman peaks attributable to Y_2O_3, SrO, CuO, or $Y_2Cu_2O_5$ are evident.[7] In the absence of detailed

TABLE I. X-ray diffraction pattern of Y-Sr-Cu-O.

2θ	Intensity	2θ	Intensity	2θ	Intensity
21.70	22	44.70	43	60.75	16
23.05	13	45.35	11	60.90	16
25.20	10	46.40	24	61.30	15
25.40	15	46.80	20	61.45	15
27.05	19	47.60	25	62.25	13
27.20	16	47.75	27	62.70	15
28.55	12	49.20	12	63.00	30
29.90	69	49.35	11	63.20	23
30.50	100	51.00	13	63.45	20
31.25	47	51.75	11	63.60	13
31.45	66	52.20	19	66.00	10
31.60	76	53.45	24	67.60	18
34.40	40	53.70	24	68.45	17
35.80	31	54.15	17	69.95	11
38.30	27	54.70	26	71.40	10
38.75	23	55.05	17	72.25	6
39.05	19	55.55	20	72.95	10
39.15	20	56.10	12	74.50	10
39.35	22	57.50	11	75.80	10
39.40	22	58.05	10	78.60	9
39.85	13	59.25	28	79.20	13
41.10	8	59.35	28	79.35	13
44.10	48	59.85	12	79.95	11

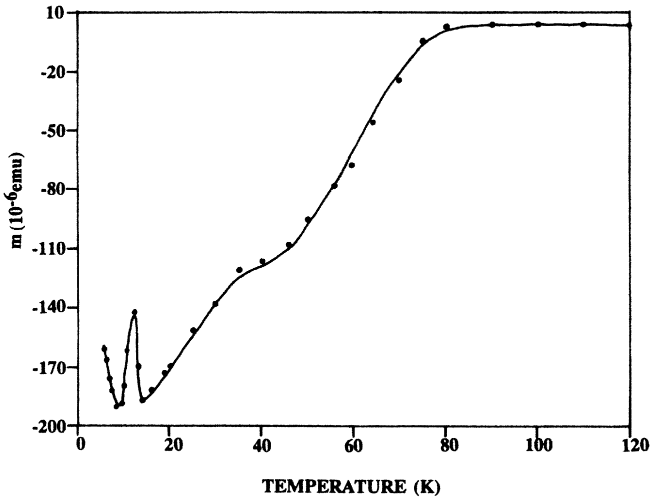

FIG. 2. Magnetic moment as a function of temperature at 10 G.

structural analysis of our samples, we tentatively assign the 80-K superconducting phase to the $YSr_2Cu_3O_y$ phase, and the 40-K phase to the 2:1:4 phase.

The 80-K superconducting phase did not form when our samples were processed at a lower temperature. This indicates that the 80-K phase is thermodynamically stable only at higher temperatures. In this regard, recall our recent conversion of the Y_2BaCuO_5 phase to the corresponding 1:2:3 phase with good superconducting characteristics by processing at 1300 °C.[5] Our Y-Sr-Cu-O sample is quite different from that of Mei, Green, Jiang, and Luo[4] who reported superconductivity at 40 K in a sample with a nominal composition of $Y_{0.3}Sr_{0.7}CuO_{3-y}$ which was processed at a temperature of about 900 °C. The superconductivity transition was rather broad, and has a width of about 20 K.

In addition to the two superconducting transitions, the magnetic-moment curve shows an anomaly at low temperatures. m shows a maximum at 14 K and then an abrupt increase at 10 K. This anomalous behavior was observed in both the cooling and heating cycles of the magnetic-moment measurements, and at several different field strengths. This anomaly may be due to magnetic coupling rather than a structural change because it was not observed in the resistance measurements. The similarity of the anomaly to that observed in $ErRh_4B_4$ (Ref. 8) indicates the existence of a magnetic ordering, either ferromagnetic or antiferromagnetic, at low temperatures. The magnetic-moment measurements at 1 kOe indicated that a paramagnetic state exists at both the high- and the low-temperature regions, and a superconducting state at intermediate temperatures. This result might suggest that the low-temperature magnetic order is due to unidentified phases present in the Y-Sr-Cu-O sample. However, the absence of evidence for magnetic components in scanning electron microscopy (SEM) microanalysis and the absence of peaks due to impurity phases in Raman spectra do not support such a suggestion. Further studies on this anomaly are currently underway, and will be reported later. It is noted that Sun *et al.*[9] earlier observed a similar anomaly in the multiphase Y-Ba-Cu-O system, which they attributed to an antiferromagnetic order.

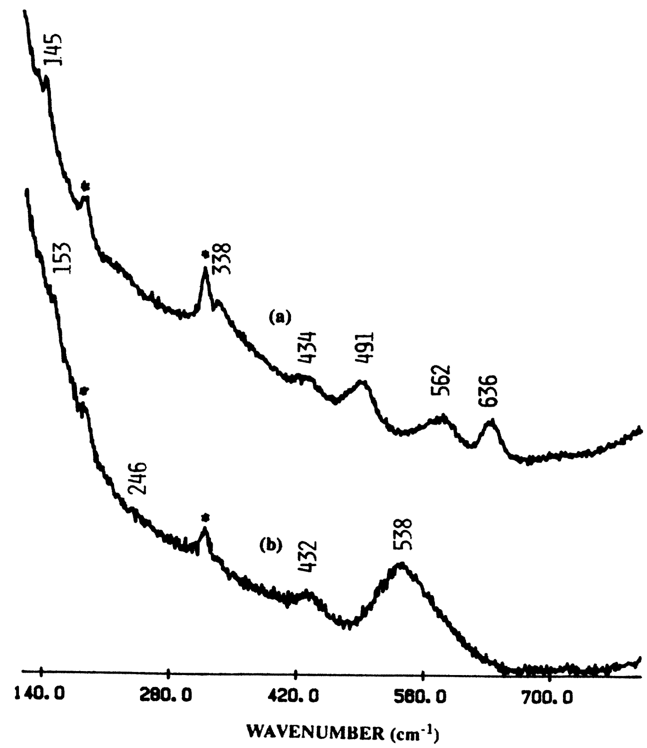

FIG. 3. Raman spectra of (a) $YBa_2Cu_3O_7$ and (b) $YSrCuO_{4-y}$.

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