

## Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure

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A stable and reproducible superconductivity transition between 80 and 93 K has been unambiguously observed both resistively and magnetically in a new Y-Ba-Cu-O compound system at ambient pressure. An estimated upper critical field  $H_{c2}(0)$  between 80 and 180 T was obtained.

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The search for high-temperature superconductivity and novel superconducting mechanisms is one of the most challenging tasks of condensed-matter physicists and material scientists. To obtain a superconducting state reaching beyond the technological and psychological temperature barrier of 77 K, the liquid-nitrogen boiling point, will be one of the greatest triumphs of scientific endeavor of this kind. According to our studies,<sup>1</sup> we would like to point out the possible attainment of a superconducting state with an onset temperature higher than 100 K, at ambient pressure, in compound systems generically represented by  $(L_{1-x}M_x)_aA_bD_y$ . In this Letter, detailed results are presented on a specific new chemical compound system with  $L=Y$ ,  $M=Ba$ ,  $A=Cu$ ,  $D=O$ ,  $x=0.4$ ,  $a=2$ ,  $b=1$ , and  $y \leq 4$  with a stable superconducting transition between 80 and 93 K. For the first time, a "zero-resistance" state ( $\rho < 3 \times 10^{-8}$   $\Omega$ -cm, an upper limit only determined by the sensitivity of the apparatus) is achieved and maintained at ambient pressure in a simple liquid-nitrogen Dewar.

In spite of the great efforts of the past 75 years since the discovery of superconductivity, the superconducting transition temperature  $T_c$  has remained until 1986 below 23.2 K, the  $T_c$  of  $Nb_3Ge$  first discovered<sup>2</sup> in 1973. In the face of this gross failure to raise the  $T_c$ , nonconventional approaches<sup>3</sup> taking advantage of possible strong nonconventional superconducting mechanisms<sup>4</sup> have been proposed and tried. In September 1986, the situation changed drastically when Bednorz and Müller<sup>5</sup> reported the possible existence of percolative superconductivity in  $(La_{1-x}Ba_x)Cu_{3-\delta}$  with  $x=0.2$  and 0.15 in the 30-K range. Subsequent magnetic studies<sup>6-8</sup> confirmed that high-temperature superconductivity indeed exists in this system. Takagi *et al.*<sup>9</sup> further attributed the observed superconductivity in the La-Ba-Cu-O system to the  $K_2NiF_4$  phase. By the replacement of Ba with Sr,<sup>8,10,11</sup> it is found that the La-Sr-Cu-O system of the  $K_2NiF_4$  structure, in general, exhibits a higher  $T_c$  and a

sharper transition. A transition width<sup>10</sup> of 2 K and an onset<sup>11</sup>  $T_c$  of 48.6 K were obtained at ambient pressure.

Pressure<sup>8,12</sup> was found to enhance the  $T_c$  of the La-Ba-Cu-O system at a rate of greater than  $10^{-3}$  K bar<sup>-1</sup> and to raise the onset  $T_c$  to 57 K, with a "zero-resistance" state<sup>13</sup> reached at 40 K, the highest in any known superconductor until now. Pressure reduces the lattice parameter and enhances the  $Cu^{+3}/Cu^{+2}$  ratio in the compounds. This unusually large pressure effect on  $T_c$  has led to suggestions<sup>8,12</sup> that the high-temperature superconductivity in the La-Ba-Cu-O and La-Sr-Cu-O systems may be associated with interfacial effects arising from mixed phases; interfaces between the metal and insulator layers, or concentration fluctuations within the  $K_2NiF_4$  phase; strong superconducting interactions due to the mixed valence states; or yet a unidentified phase. Furthermore, we found that when the superconducting transition width is reduced by making the compounds closer to the pure  $K_2NiF_4$  phase, the onset  $T_c$  is also reduced while the main transition near 37 K remains unchanged. Extremely unstable phases displaying signals indicative of superconductivity in compounds consisting of phases in addition to or other than the  $K_2NiF_4$  phase have been observed by us,<sup>8,14</sup> up to 148 K, but only in four samples, and in China,<sup>15</sup> at 70 K, in one sample. Therefore, we decided to investigate the multiple-phase Y-Ba-Cu-O compounds instead of the pure  $K_2NiF_4$  phase, through simultaneous variation of the lattice parameters and mixed valence ratio of Cu ions by chemical means at ambient pressure.

The compounds investigated were prepared with nominal compositions represented by  $(Y_{1-x}Ba_x)_2CuO_{4-\delta}$  with  $x=0.4$  through solid-state reaction of appropriate amounts of  $Y_2O_3$ ,  $BaCO_3$ , and  $CuO$  in a fashion similar to that previously described.<sup>8</sup> Bar samples of dimensions  $1 \times 0.5 \times 4$  mm<sup>3</sup> were cut from the sintered cylinders. A four-lead technique was employed for the resistance ( $R$ ) measurements and an ac inductance bridge for the mag-

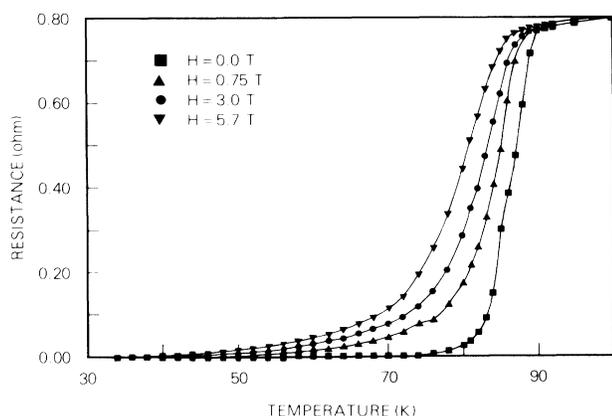


FIG. 1. Temperature dependence of resistance determined in a simple liquid-nitrogen Dewar.

netic susceptibility ( $\chi$ ) determinations. The temperature was measured by means of Au+0.07% Fe-Chromel and Chromel-Alumel thermocouples in the absence of a magnetic field, and a carbon-glass thermometer in the presence of a field. The latter was calibrated against the former without a field. Magnetic fields up to 6 T were generated by a superconducting magnet.

The temperature dependence of  $R$  determined in a simple liquid-nitrogen Dewar is shown in Fig. 1.  $R$  initially drops almost linearly with temperature  $T$ . A deviation of  $R$  from this  $T$  dependence is evident at 93 K and a sharp drop starts at 92 K. A "zero- $R$ " state is achieved at 80 K. The variation of  $\chi$  with  $T$  is shown in Fig. 2. It is evident that a diamagnetic shift starts at 91 K and the size of the shift increases rapidly with further cooling. At 4.2 K, the diamagnetic signal corresponds to 24% of the superconducting signal of a Pb sample with similar dimensions. In a magnetic field, the  $R$  drop is shifted toward lower  $T$ . At our maximum field of 5.7 T, the "zero- $R$ " state remains at a  $T$  as high as 40 K. Pre-

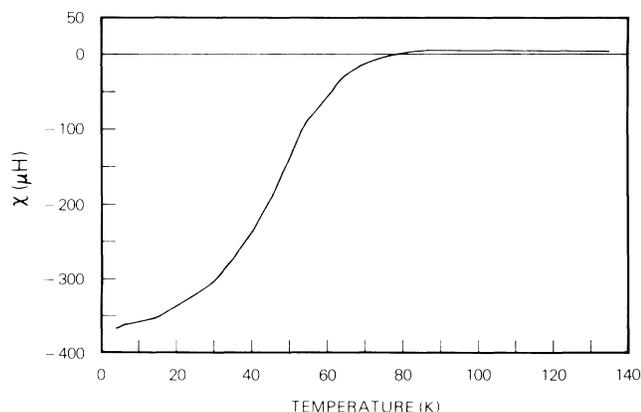


FIG. 2. Temperature dependence of magnetic susceptibility.

liminary x-ray powder diffraction patterns show the existence of multiple phases uncharacteristic of the  $K_2NiF_4$  structure in the samples. Detailed analyses are under way.

The above results demonstrate unambiguously that superconductivity occurs in the Y-Ba-Cu-O system with a transition between 80 and 93 K. We have determined the upper critical field  $H_{c2}(T)$  resistively. If the positive curvature at very low fields is neglected, one gets a value of  $dH_{c2}/dT$  near  $T_c$  of 3 T/K or 1.3 T/K, depending on whether  $H_{c2}(T_c)$  is taken at the 10% or the 50% drop from the normal-state  $R$ . In the weak-coupling limit,  $H_{c2}(0)$  is thus estimated to be between 80 and 180 T in the Y-Ba-Cu-O system investigated. We believe that the value of  $H_{c2}(0)$  can be further enhanced as the material is improved. The paramagnetic limiting field at 0 K for a sample with a  $T_c \sim 90$  K is 165 T. Because of the porous and multiphase characteristics of the samples, it is therefore difficult to extract any reliable information about the density of states from the slope of  $H_{c2}(T)$  at  $T_c$  on the basis of the dirty-limit approximation.

On the basis of the existing data, it appears that the high-temperature superconductivity above 77 K reported here occurs only in compound systems consisting of a phase or phases in addition to or other than the  $K_2NiF_4$  phase. While it is tempting to attribute the superconductivity to possible nonconventional superconducting mechanisms as mentioned earlier, all present suggestions are considered to be tentative at best, especially in the absence of detailed structural information about the phases in the Y-Ba-Cu-O samples. However, we would like to point out here that the lattice parameters, the valence ratio, and the sample treatments all play a crucial role in achieving superconductivity above 77 K. The role of the different phases present in superconductivity is yet to be determined.

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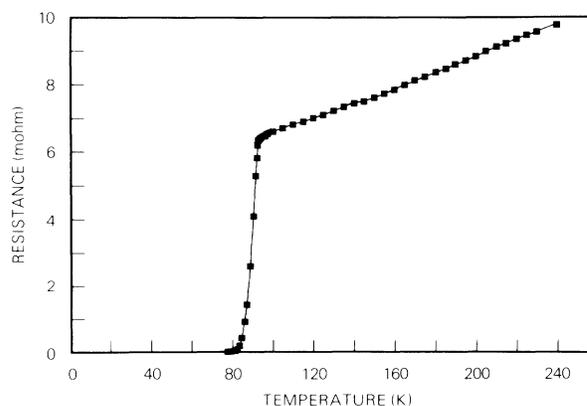


FIG. 3. Magnetic field effect on resistance.

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<sup>15</sup>According to a report in Renmin Ribao, 17 January 1987.