# High-Pressure Study of the New Y-Ba-Cu-O Superconducting Compound System

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The pressure effect on the superconducting state above 77 K in the new Y-Ba-Cu-O compound system has been determined. In strong contrast to what is observed in the La-Ba-Cu-O and La-Sr-Cu-O systems, pressure has only a slight effect on the superconducting transition temperature.

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Recently, Bednorz and Müller reported[1] the possible existence of superconductivity up to 35 K in the La-Ba-Cu-O compound system. The significance of the $K_2NiF_4$ phase present in their samples was also pointed out. Subsequent magnetic measurements,[2-4] indeed, confirmed the report, and the observed superconductivity was attributed[5] to the $K_2NiF_4$ phase. Pressure[4,6] was found to enhance the superconducting transition temperature $T_c$ of La-Ba-Cu-O at a rate of greater than $10^{-3}$ K bar$^{-1}$ and to raise[7] the onset $T_c$ to 57 K, reaching a "zero-resistance" state at 40 K, the highest in any known superconductor until now. Replacement[4,8,9] of Ba ions by smaller Sr ions in La-Ba-Cu-O compounds of the $K_2NiF_4$ structure was also found to enhance the $T_c$ and sharpen the transition. A transition width[8] of 2 K and an onset[9] $T_c$ of 48.6 K were obtained at ambient pressure. On the other hand, we found that when the superconducting transition width is reduced by making the compound with a purer and more homogeneous $K_2NiF_4$ phase, the onset $T_c$ is usually reduced while leaving the main transition at ~37 K unchanged. Furthermore, extremely unstable and difficult-to-reproduce phases exhibiting electrical and magnetic signals indicative of superconductivity up to 148 K at ambient pressure have been observed by us[4,10] in only four samples consisting of more than one phase and often not including the $K_2NiF_4$ or the $ABO_3$ perovskite as the major phase. Workers in China[11] also reported observing signs of superconductivity in one of the mixed-phase samples at 70 K. This led us to the proposition[12] that $T_c$ above 77 K may exist in compound systems represented generically by the formula $(L_{1-x}M_x)_aA_bD_y$ and not necessarily the pure $K_2NiF_4$ phase. As shown in the preceding paper,[13] superconductivity above 77 K is achieved at ambient pressure when $L=Y$, $M=Ba$, $A=Cu$, and $D=O$ with nominal compositions $a=2$, $b=1$, $x=0.4$, and $y=4-\delta$, where $\delta$ is undetermined.

In an attempt to probe the nature of the superconductivity observed, we have determined the hydrostatic effects on $T_c$ of the Y-Ba-Cu-O compound system, respectively, up to 19 kbar. $T_c$ of Y-Ba-Cu-O was affected only slightly by pressure in strong contrast to what is observed for the $K_2NiF_4$ phase in La-Ba-Cu-O and La-Sr-Cu-O. This, together with our preliminary x-ray powder diffraction data, suggests that the Y-Ba-Cu-O compound system displaying superconductivity above 77 K may be very different from the superconducting La-Ba-Cu-O and La-Sr-Cu-O systems which have only a maximum onset[9] of 48.6 K at ambient pressure.

The compounds examined were the same as those described in the preceding paper.[13] They were prepared with nominal compositions represented by $(Y_{1-x}Ba_x)_2$-$CuO_{4-\delta}$ 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 reported.[4] The powder x-ray measurements were carried out with a GE diffractometer with a resolution of ~5%. Bar samples of dimensions $1\times0.5\times4$ mm$^3$ were cut from the sintered cylinders. A standard four-lead technique was used for the resistance ($R$) measurements. The pressure environment was provided by a Be-Cu clamp with a fluid medium. The pressure was determined by a pressure gauge at room temperature. It is then corrected by subtraction of the loss due to the freezing of the pressure medium at lower temperature, i.e., $< 180$ K, estimated to be about 2 kbar. The temperature was measured by a Chromel-Alumel thermocouple situated next to the sample.

The Y-Ba-Cu-O compounds with superconductivity above 77 K clearly exhibit more than one phase when examined under an optical microscope, one dark green and the other black. No effort can be made to fit satisfactorily the diffraction patterns with the known $K_2NiF_4$ layered or $ABO_3$ perovskite phase. It is therefore evident that the Y-Ba-Cu-O compound exhibiting superconductivity above 77 K may not be identified with the well-known cubic perovskite or the tetragonal layered-structure phase at our present resolution. Detailed analyses are under way.

Typical temperature dependence of $R$ normalized to that at 100 K for simplicity is shown in Fig. 1 at a few

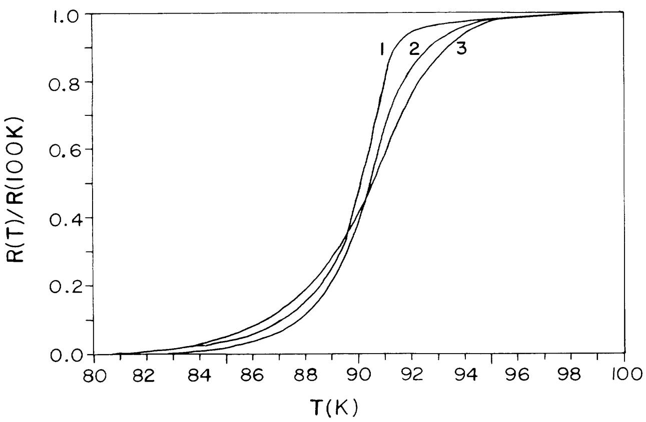


FIG. 1. The temperature dependence of resistance at different pressures: 1 = 0 kbar, 2 = 8.4 kbar, and 3 = 19 kbar.

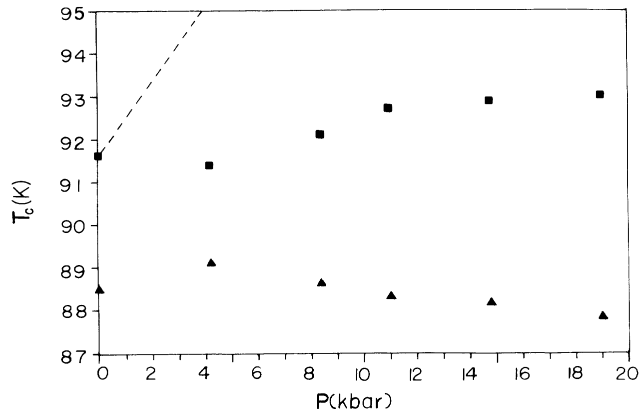


FIG. 2. The pressure effect on the superconducting transition onset temperature $T_{c0}$ (squares) and the completing temperature $T_{cf}$ (triangles) (see text for definition). The slope of the dashed line is for the $K_2NiF_4$ phase of La-Ba-Cu-O and La-Sr-Cu-O compounds.

pressures. At ambient pressure, $R$ initially decreases with temperature linearly and starts to deviate from this linear dependence at ~93 K. A "zero-$R$" state is reached at 80 K. One may define the superconducting onset temperature $T_{c0}$ and the complete temperature $T_{cf}$ as the intersection temperatures of the main part of the transition with the linear extrapolation of the $R(T)$ curve and the "zero-$R$" line, above and below the transition, respectively. Under pressure, $T_{c0}$ is shifted up slightly and $T_{cf}$ first up and then down, as shown in Fig. 2. The observation is reversible during pressure cycling when proper precautions are taken. The midpoint of the transition, i.e, where $R(T)/R(100\ \mathrm{K}) = 0.5$, changes only slightly. This is in strong contrast to that observed[4,6,7] previously in the $K_2NiF_4$ phase of the La-Ba-Cu-O and La-Sr-Cu-O systems with a maximum $T_{c0} \sim 48.6$ K at ambient pressure. The pressure effects on these latter systems are represented by a dashed line also shown in Fig. 2 for comparison.

In conclusion, we have found that pressure has little effect on the superconducting state of Y-Ba-Cu-O, in strong contrast to the behavior of the $K_2NiF_4$-phase La-Ba-Cu-O and La-Sr-Cu-O systems. This may be due to chemical pressure associated with the smaller Y atoms already present in Y-Ba-Cu-O. Preliminary x-ray powder-diffraction results indicate that the high-temperature superconductivity in Y-Ba-Cu-O can only be attributed to one or more phases with structures different from the cubic perovskite or tetragonal layered one. The detailed structures of Y-Ba-Cu-O displaying superconductivity above 77 K are being determined. We believe that the transition can be further sharpened by adjustment of the various physical and chemical parameters.

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