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Superconductivity at 90 K in the Y-Ba-Al-Cu-O System

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The addition of small quantities of Al atoms to the Y-Ba-Cu-O system has been studied. A superconducting transition at 90 K has been observed in a new Y-Ba-Al-Cu-O compound system, by resistance measurements. The superconductivity is stable and reproducible after several heat cycles.

Recently Bednorz and Müller[1] reported that the Ba-La-Cu-O system with the composition $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ with $x=1$ and 0.75 became superconducting below 13 K; the most interesting fact they reported was that, in their resistivity measurements, the resistivity started to decrease near 30 K as the temperature was lowered. An intensive research effort appeared shortly after superconductivity in this system was confirmed by magnetic susceptibility measurements.[2,3] By careful sample preparation Takagi *et al.*[4] attributed the observed superconductivity in the La-Ba-Cu-O system to the K_2NiF_4-type structure. They also reported that the substitution of Ba for La led to the Cu-mixed-valence state, Cu^{2+}-Cu^{3+}, and that this mixed-valence can play an important role in the mechanism of the high-T_c superconductivity in that system. Chu *et al.*[5] found that hydrostatic pressure, in compounds with nominal compositions given by $(La_{0.9}Ba_{0.1})_2CuO_{4-\delta}$ enhanced the onset of the superconducting transition to 52 K. They suggested that the high temperature superconductivity can be associated with interfaces due to mixed phases or concentration fluctuations, mixed-valence-dependent electron-pairing interaction or a d-f mixing. With the replacement of Ba by Sr,[6-8] that is for the La-Sr-Cu-O system in the K_2NiF_4 structure, superconductivity onset was found at 48.6 K with a transition width of 2 K, at ambient pressure. More recently Wu *et al.*[9] reported the occurrence of superconductivity in the Y-Ba-Cu-O system with nominal compositions represented by $(Y_{1-x}Ba_x)_2CuO_{4-\delta}$ with $x=0.4$, in which the onset of superconductivity was at 93 K and the zero resistivity state was achieved at 80 K. In a subsecuent paper[10] they reported that in the Y-Ba-Cu-O system pressure had only a slight effect on the superconducting transition temperature, in contrast to what is observed for the K_2NiF_4 phase in La-Ba-Cu-O system. They suggested that this may be due to chemical pressure associated with the smaller Y atoms already present in Y-Ba-Cu-O; they also suggested, from their results together with their preliminary X-ray powder diffraction data, that the system displaying superconductivity in Y-Ba-Cu-O could be different from that of the La-Ba-Cu-O and La-Sr-Cu-O systems. High-T_c superconductivity in the Y-Ba-Cu-O system has also been reported independently by other groups.[11-14]

Considering the ionic radii of La and Y on the one hand and those of Ba and Sr on the other, we studied the addition of Al atoms in the Y-Ba-Cu-O system. We took into account the results of Hoggins *et al.*[15] that in a Ba-Fe-S compound system Al atoms replaced the Ba atoms in such a way that the Ba^{+2} ion is replaced by an $(Al\text{-}e)^{+2}$ unit, maintaining the charge balance by the reduction of the Fe atoms. In this letter we report the occurrence of high-T_c superconductivity in the Y-Ba-Al-Cu-O compound system from resistivity measurements.

The compounds investigated were prepared with nominal compositions represented by $(Y_{1-x-y}Ba_xAl_y)_2CuO_4$, through the reaction of appropriate amounts of Y, $BaCO_3$, CuO and Al_2O_3. The mixture was first calcined at 1000°C for 1 h, then ground and calcined again at 1000°C for 24 h. For sample preparation the calcined powders were homogenized by grinding, cold-pressed into disk shapes and then sintered in an oven that was previously heated to 1100°C; the current in the oven was then turned off to let the sample cool down slowly to 500°C. All the heat treatments were conducted in air.

Disk-shaped samples of 1.2 cm diameter and about 0.18 cm thick were cut in two and the resistance measurements were made with a bridge having a low resistance sensitivity of $10^{-7}\,\Omega$, by the usual four-point-probe technique using silver paint contacts. The measurements between 300 K and 10 K were performed in a continuous-flow cryostat (Air Products) connected to a microcomputer (HP 9845B) to give a fully automatic system for temperature variation, data acquisition and processing.

Figure 1 shows the resistance-temperature characteristics of a sample prepared with nominal composition $(Y_{0.6}Ba_{0.32}Al_{0.08})_2CuO_{4-\delta}$ which shows a broad transition starting at $T_{co}=90$ K and reaching the zero-resistance state at $T_c=22.5$ K. This sample shows a semiconductor type resistivity as a function of temperature before it reaches the superconducting state. Figure 2 shows the resistance-temperature characteristics of a sample with nominal composition given by $(Y_{0.6}Ba_{0.35}Al_{0.05})_2CuO_{4-\delta}$, which shows a metallic type resistance characteristic before the transition and has a smaller transition width compared with the previous one, starting at $T_{co}=90$ K

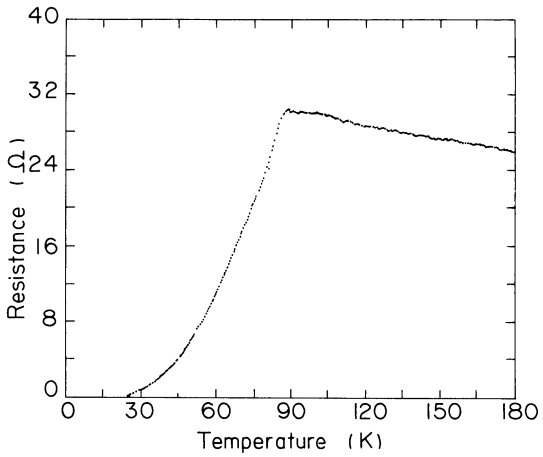

Fig. 1. Resistance as function of temperature for the sample prepared with nominal composition $(Y_{0.6}Ba_{0.32}Al_{0.08})_2CuO_{4-\delta}$.

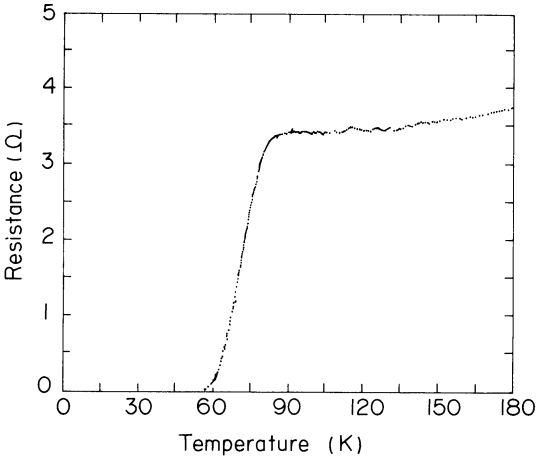

Fig. 2. Resistance as function of temperature for the sample prepared with nominal composition $(Y_{0.6}Ba_{0.35}Al_{0.05})_2CuO_{4-\delta}$.

and reaching the complete superconducting state at $T_c = 58$ K.

The presence of superconductivity at 90 K in the Y-Ba-Al-Cu-O system seems to be significant for the following reasons. First, the inclusion of Al in the Y-Ba-Cu-O system does not significantly much affect the onset of the superconducting state as compared to the onset reported by Wu *et al.*[9] Secondly, from our experience we found that including Al in the Y-Ba-Cu-O system relaxes greatly the tight restrictions on the conditions of preparation of superconducting compounds. Thirdly, the knowledge that Al can be included could be important from the technological point of view. Studies are under way to identify the superconducting phase, as well as to investigate the dependence of T_c on various parameters, as Al composition, Ba composition and annealing conditions.

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