Superconductivity in the system $(Al_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$

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High-temperature superconductivity was observed in the system $(Al_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ for $0 \leq x \leq 0.85$. Transition temperatures at zero resistance vary between 90.6 and 50 K, and are related to gradual crystal lattice changes. At $x=0.90$ a time- and current-dependent resistance is found for $T < 25$ K.

High-temperature superconductivity was reported by Bednorz and Müller[1] in the system La-Ba-Cu-O, and later in the system Y-Ba-Cu-O by Wu *et al.*[2] and others.[3] In the Y-based system high-temperature superconductivity with transition temperatures near 91 K was attributed[4] to the compound $Y_1Ba_2Cu_3O_{6.5+\delta}$, with δ between 0.2 and 0.5, and this phase was crystallographically identified by LePage *et al.*,[5] Hazen *et al.*,[6] and Grant *et al.*[7] Substitution of Y by the series of rare-earth metals gave essentially similar results to those for the yttrium-based compounds.[8-10]

In this work, we present the results of a systematic investigation of the substitution of Y by the non-transition-metal Al. Such a substitution was suggested by the similarity in the chemistry of Al and Y. Al, however, has a much smaller ionic radius, 0.51 Å, compared to that of Y, 0.97 Å. It was therefore not clear to what degree Al could be introduced into the Y-based compound without major crystallographic changes. It was found from x-ray powder diagrams, that the substitution of Y by Al produces only gradual changes in the lattice structure up to a molar concentration of $x=0.90$. Electric resistance measurements showed that all samples are superconducting for $0 \leq x \leq 0.85$. Complete Al substitution, however, leading to the compound of nominal composition $Al_1Ba_2Cu_3O_{6.5+\delta}$, produces an insulator at 77 K. The electric resistivity displays over this range of Al substitution gradual and systematic changes between the "ideal" behavior of $Y_1Ba_2Cu_3O_{6.5+\delta}$, and marginally superconducting behavior at high substitution values.

Samples of $(Al_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ were prepared using Al_2O_3 powder (Al_2O_3, Merck, type 60/E), Y_2O_3 (Morton Thiokol, Inc., 99.99%), $BaCO_3$ (Baker Analyzed Reagent Grade) and CuO (Fisher Reagent Grade). The powders were ground and mixed, formed into a pellet of diameter 1.27 cm, and approximately 2 mm thickness and reacted in air at 880 °C for 23 h. After this the pellets were reground, new pellets formed, and sintered in flowing O_2 for 7 h at 925 °C. The product was furnace cooled for 12 h at an initial rate of 200 °C/h.

Electrical resistance was measured as a function of temperature using the standard four-terminal technique. Temperature was determined by a Pt thermometer calibrated to a precision of ± 20 mK. Four pressed indium contacts were applied to the pellets. Measuring current densities of around 0.03 A/cm^2 were used. We are reporting resistances rather than resistivities because of the distributed geometry of the samples. An approximate conversion from resistance (in Ω) to resistivity (in Ω cm) can be obtained by multiplying the resistance data with 0.07.

In Fig. 1 we show the resistance data as function of aluminum concentration. For the pure Y case, $x=0$, we find a transition temperature of 90.6 K, and transition

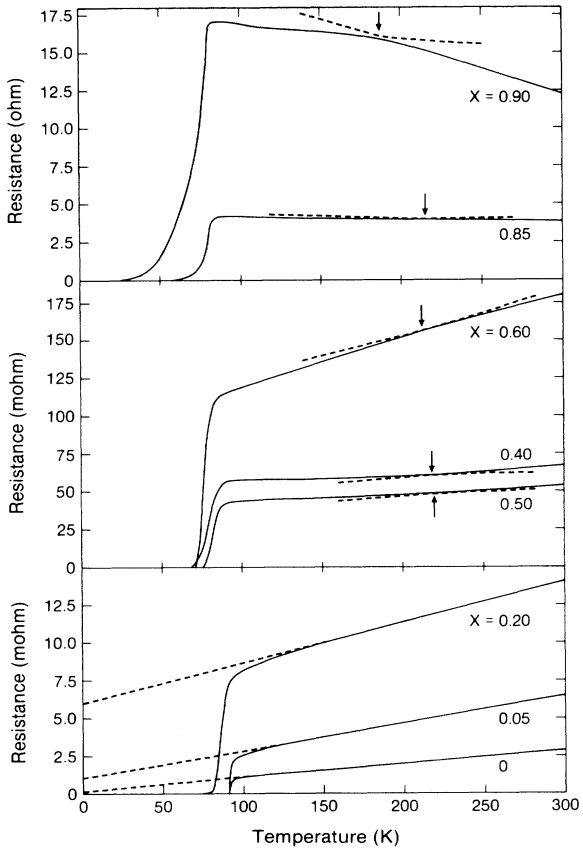

FIG. 1. Electric resistance of $(Al_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ as a function of temperature and Al concentration x. The high-temperature resistance is fitted to straight lines, the changeover between the two linear regions is indicated by an arrow. Resistance can be approximately converted to resistivities (in Ω cm) by multiplication with 0.07.

width of about 1.5 K. The high-temperature resistance is exactly linear in temperature. There is a small positive axis intercept of the extrapolated linear resistance at 0 K, corresponding to a resistance ratio of $R^L(0)/R(300) = 0.07$, where $R(300)$ is the resistance at 300 K, and $R^L(0)$ the extrapolated resistance at 0 K. Introduction of aluminum has the effect of gradually raising the room-temperature resistance from about 2.5 mΩ to 12.5 Ω, for the geometry of our samples. For x up to 0.20, the high-temperature behavior is still linear in temperature, but the 0-K axis intercept increases, as well as the width of the transition and the first deviations from linearity. For $x = 0.20$ we find $R^L(0)/R(300) = 0.43$. The resistance has dropped to 50% of the extrapolated linear resistance at 86 K, and the zero-resistance transition occurs at 80 K, this gives an indication of the large transition width in this case. The first deviation from linearity is found at 145 K. For other samples of this Al concentration we observed deviations from linearity as high as 190 K, this point is quite sensitive to the annealing conditions. For aluminum contents of 30% and larger, we find that the high-temperature resistance is composed of two linear regions. The changeover occurs near 220 K for all aluminum concentrations up to $x = 0.85$; at $x = 0.90$ this point has dropped to 180 K. We have observed these linear resistance regions in all samples which show a low-temperature drop in resistance.

For aluminum concentrations of 0.70 and above, the high-temperature resistance is still composed of two linear regions, but the resistance at room temperature rises with falling temperature. For $x \geq 0.7$ we also observe a small rise in resistance before the low-temperature resistance drop, probably due to localization.[11,12] The transition width becomes quite large for $x = 0.85$ and 0.90. For $x = 0.85$ we still observe a true zero-resistance state below $T_c^{R=0} = 50$ K. For $x = 0.90$, however, in spite of the similarity in the resistance behavior, such a state is not reached. The resistance in this sample drops by a factor 4400 between 90 and 30 K. Below 25 K this sample shows a resistance which increases both with time and measuring current.This behavior suggests polarization of the conduction system by the measuring current. This sample is therefore at the margin of superconductivity. For $x = 0.95$ and $x = 1.00$ we found a resistance rapidly, and nonlinearly, rising from room temperature, both samples are insulators at 77 K.

In Fig. 2 we show the transition temperature at zero resistance, $T_c^{R=0}$, as a function of aluminum concentration. The transition temperature drops from near 91 to 62 K for $x = 0.40$. At $x = 0.50$, however, we find an increase of transition temperature to 73 K, and then again a gradual decrease with increasing aluminum content to $T_c^{R=0} = 50$ K for $x = 0.85$. The changes in transition temperature appear to be connected to systematic changes in the crystal structure of the samples.

X-ray powder diagrams were taken from all samples on which resistance measurements were made, using a Rigaku Geiger-Flex diffractometer with Co$K\alpha_{1+2}$ radiation. Overall spectra are shown in Fig. 3. The typical spectrum of $Y_1Ba_2Cu_3O_{6.5+\delta}$ is undergoing systematic and gradual changes with increasing aluminum content.

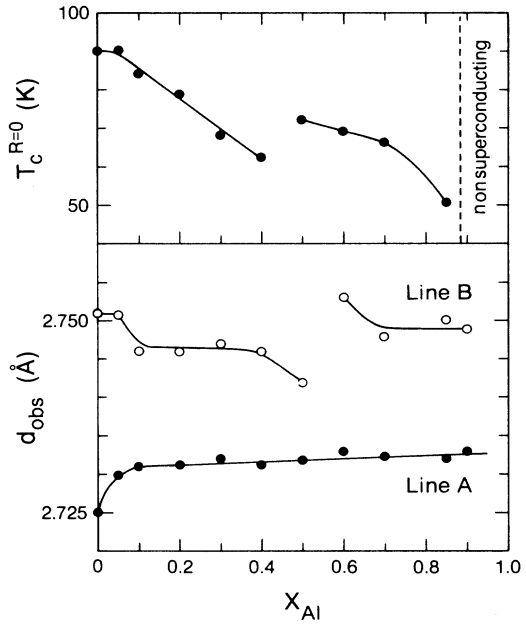

FIG. 2. Superconducting transition temperature (zero resistance) $T_c^{R=0}$ as function of Al concentration (upper figure). Observed planar spacing of the high intensity doublet (lower figure). *A* line [(103) and (110)], and *B* line [(013)], indexed in the tetragonal cell.

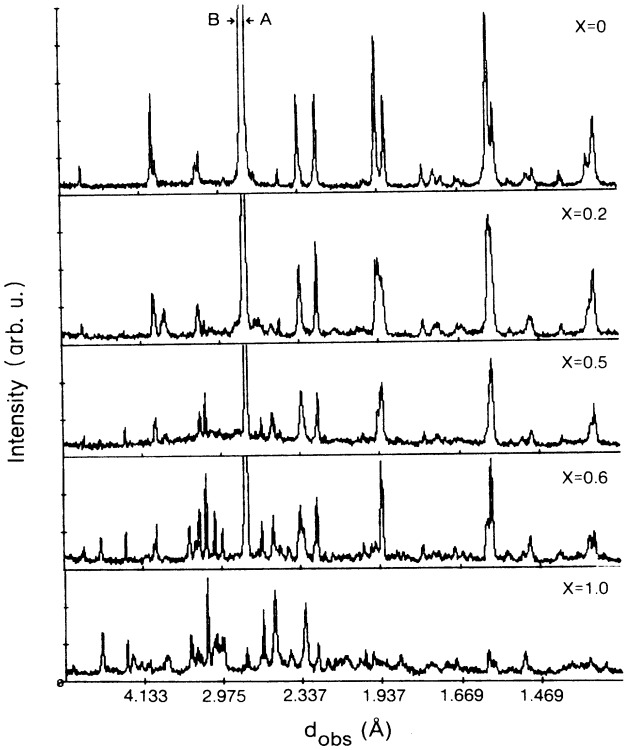

FIG. 3. X-ray powder diagram for Al concentrations between $x = 0$ and $x = 1.00$

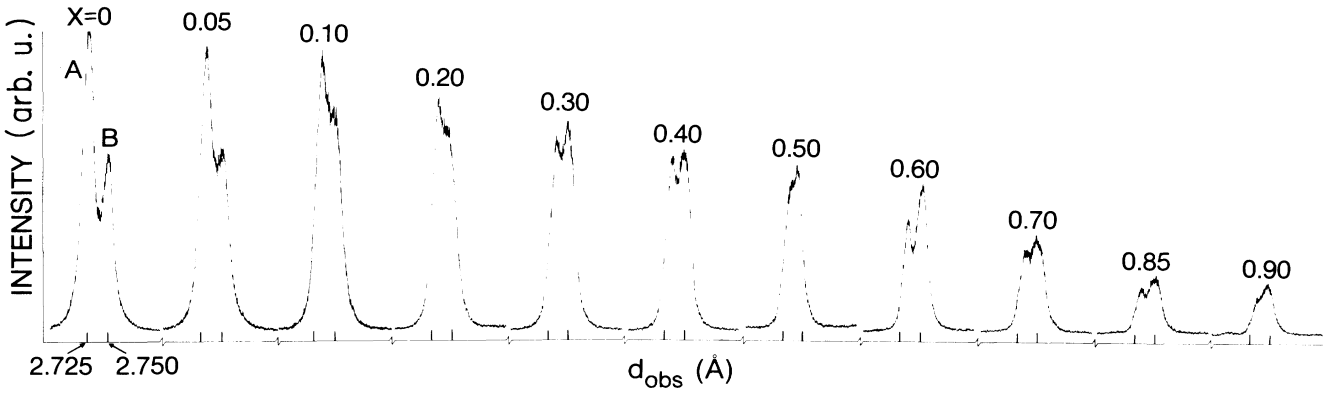

FIG. 4. High-resolution powder diagram of the A and B lines near 2.725 and 2.750 Å, as a function of Al concentration x.

From $x=0.30$ on there are some indications of the presence of the pure aluminum phase, $Al_1Ba_2Cu_3O_{6.5+\delta}$, in the spectra, so that these samples are two phase. The changes in the spectrum with the addition of aluminum are most pronounced in the doublet at d spacings near 2.725 Å [$(hkl)=(103)$ and (110)], and 2.750 Å [(013)]; at 1.9479 Å [(020) and (006)], and 1.910 Å [(200)]; and at 1.583 Å [(123) and (116)], and 1.571 Å [(213)]. Indexation is in the tetragonal cell. The highest intensity doublet is shown in more detail in Fig. 4 as a function of aluminum concentration. The splitting between the A line (2.725 Å) and the B line (2.750 Å) of this doublet which is caused by the orthorhombic distortion of the tetragonal cell, is seen to change toward smaller splitting and therefore less distortion, with increasing aluminum content. Between $x=0.50$ and $x=0.60$ this splitting increases again to its original value. The doublet at 1.947 and 1.910 Å first broadens and then becomes quite narrow, and similar changes are seen in the doublet at 1.583 and 1.571 Å. Increasing aluminum content, therefore, decreases the orthorhombic distortion up to $x=0.50$, but this is restored for larger concentrations to its original value. Other changes throughout the spectrum indicate, however, that other lattice changes also occur, which still have to be analyzed.

In Fig. 2 we compare the splitting of the high-intensity doublet with the transition temperature as a function of aluminum content. It is quite clear that the transition temperature changes are due to changes in the crystal lattice. Smaller orthorhombic distortion leads to lower transition temperatures, as was found also in other high-T_c superconductors.[13]

In conclusion, we find high-temperature superconductivity, resistively determined, in samples of $(Al_xY_{1-x})Ba_2Cu_3O_{6.5+\delta}$ for $0\leq x\leq 0.85$. The changes in transition temperature and high-temperature dependence of resistance are related to gradual changes of the crystal lattice with aluminum concentration. For $x=0.90$ we observe a time- and current-dependent resistance at low temperatures.

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