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Effect of Mn on the superconductivity of $YBa_2Cu_3O_{7-\delta}$

R. F. Jardim, S. Gama, O. F. de Lima, and I. Torriani
Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas (UNICAMP),
13081 Campinas, São Paulo, Brazil

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We have prepared samples of $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$, with $x = 0.0$, 0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20. Superconductivity with T_c in the range 84–92 K is demonstrated by resistivity and magnetic susceptibility measurements. The substitution of Mn for Cu did not affect the onset temperature for the resistivity transition. X-ray diffraction analysis revealed the presence of additional phases, the amount increasing with Mn content, and also a slight modification of the $YBa_2Cu_3O_{7-\delta}$ lattice parameters. A strong correlation between the width of the superconducting transition and the presence of additional phases was observed.

Superconductivity above 90 K has been reported in the mixed-phase system Y-Ba-Cu-O.[1] It was suggested that high-critical temperature (T_c) might arise from interfacial interactions between different phases. On the other hand, a single superconducting phase was found in Y-Ba-Cu-O compounds by Cava *et al.*[2] They have identified this phase as $YBa_2Cu_3O_{7-\delta}$ which can be described as an orthorhombic, distorted, oxygen-deficient perovskite. The substitution of Y in this compound by most rare-earth elements did not affect T_c (Refs. 3 and 4) and this has led to the conclusion that a common feature of high-T_c oxides is the quasi-two-dimensional motion of carriers within Cu-O planes.[5–7] Substitution of Cu by metallic elements in these materials is of interest in the light of different pairing mechanisms recently discussed.[8–10] Pan *et al.*[11] have prepared the mixture $YBa_2Ag_3O_7$ and observed conductivity with T_c onset at 50 K and a transition width of about 30 K; Xiao *et al.*[12] have studied samples of $YBa_2(Cu_{1-x}A_x)_3O_7$ where A is one $3d$ transition metal. Experiments reporting other substitutions are described in Refs. 13 and 14.

Our aim in this paper is to study how the substitution of Mn, an antiferromagnetic element, for Cu changes the superconducting properties of the $YBa_2Cu_3O_{7-\delta}$ compound. Moreover, the observed changes could shed light on the nature of the high-T_c superconductivity.

We have prepared the mixture $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$, $x = 0.0$, 0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20, by mixing appropriate proportions of Y_2O_3, $BaCO_3$, CuO, and MnO_2, all with purities of 99.9%. Powders were cold-pressed into disc-shaped pellets and calcined at 950 °C. The resultant mixture was pulverized, pressed again into disc-shaped pellets having 15-mm diameter and 4-mm height, sintered at 950 °C for 50 h in flowing oxygen, and then furnace-cooled to room temperature (50 °C/h). The samples were cut into small pieces for optical metallographic analysis, resistivity and magnetic susceptibility measurements, and x-ray-diffraction studies.

Optical metallographic analysis revealed that all samples listed showed small amounts of additional phases increasing with the Mn content.[15] However, for samples with $x = 0.0$, 0.01, and 0.025, the amount of additional phases was very small, probably below 1%. In all cases, these phases were precipitated intragranularly.

Electrical resistance was measured in small pieces of about $8.0\times3.0\times4.0\ mm^3$ by a standard dc four-terminal method with current density of $0.05\ A/cm^2$. The leads were tin soldered on contacts of deposited palladium films of about 5000-Å thickness. The temperature was measured using a calibrated thermocouple (Au-Fe)-Chromel. T_c was chosen to be the midpoint of the resistive transition.

Magnetic susceptibility was measured in an ac inductive bridge at 155-Hz exciting signal and an ac magnetic field of 3.0 Oe. In these experiments, the temperature was measured using a calibrated carbon resistor and another critical temperature was defined at the onset of the diamagnetic transition.

Figure 1 shows the dependence of T_c on Mn concentration, where the open squares represent the onset of the resistive transition, the filled squares represent the end of the resistive transition, and open circles represent the magnetic susceptibility transition. The parent composition, $YBa_2Cu_3O_{7-\delta}$, has a T_c of 92 K and a small transition width of about 2 K. It is very interesting to note that

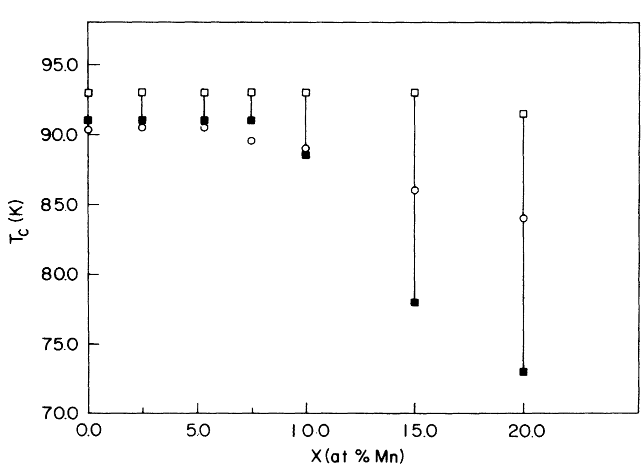

FIG. 1. The critical temperature determined from resistive and magnetic transitions plotted as a function of the Mn concentration in $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$.

the transition onset temperature (T_{onset}) and the zero-resistance temperature (T_{c0}) are constant with Mn content in the range $0 < x < 0.10$, suggesting that the Mn substitution does not cause a measurable change in T_c. On the other hand, for $x \geq 0.10$, the Mn substitution provides a significant change in T_c, although not large enough to destroy the superconductivity. Indeed, $T_{\text{onset}} \simeq 93$ K was almost invariant for all samples. Our $T_{c0} = 89$ K, for $x = 0.10$, agrees with the result reported by Prased *et al.*[16] On the other hand, our $T_c = 91$ K for that same sample disagrees with the result reported by Xiao and co-workers,[12,17] who found $T_c = 80$ K for the same composition. T_c presents a nonlinear decrease with the Mn content, and has a different behavior when compared to the zinc[17] and nickel[18] substitutions. The transition width gradually broadens probably due to the gradual occurrence of nonsuperconducting additional phases. In order to test this hypothesis, we have plotted the electrical resistivity against temperature, for $x = 0.0$, 0.05, 0.10, and 0.20, in Fig. 2. The normal-state resistivity increases with the Mn content probably due to the enhancement of carrier scattering by dispersed amounts of the intragrain additional phases.

The crystal structure of the samples was studied by x-ray diffraction using Cu *Ka* radiation. Figure 3 shows the diffractograms for all the samples. An analysis of the peak positions and intensities shows that the parent sample, $x = 0.0$, has the orthorhombic structure with lattice parameters $a = 3.823$ Å, $b = 3.886$ Å, and $c = 11.680$ Å, as given in the literature.[2,5] The other samples preserve the basic orthorhombic structure, though some modifications of the diffraction pattern are observed, as follows. Up to $x = 0.025$ Mn content, the samples appear as single phase, the orthorhombic structure of $YBa_2Cu_3O_{7-\delta}$, with practically no changes in the spectrum, this being consistent with the constant behavior of T_{onset}, T_{c0}, and T_c from magnetization, as shown in Fig. 1. For the sample with $x = 0.05$ new phases start appearing, most likely Y_2BaCuO_5, which accounts for most of the extra peaks. It is probable, however, that the 1:2:3 phase might have suffered some structural modifications, judging from the changes observed in several critical regions of the spectrum. First, we note that the splitting of the most intense peaks corresponding to the (110), (103), and (013) reflections of $YBa_2Cu_3O_{7-\delta}$, lose resolution in a fashion similar to when the sample goes through the orthorhombic-tetragonal phase transition.[19]

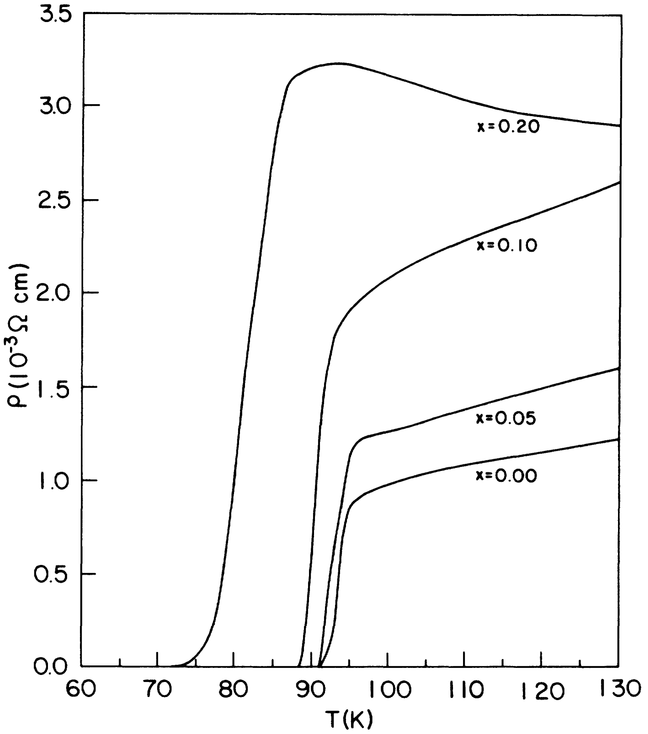

FIG. 2. Temperature dependence of the resistivity for four typical compositions of $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$.

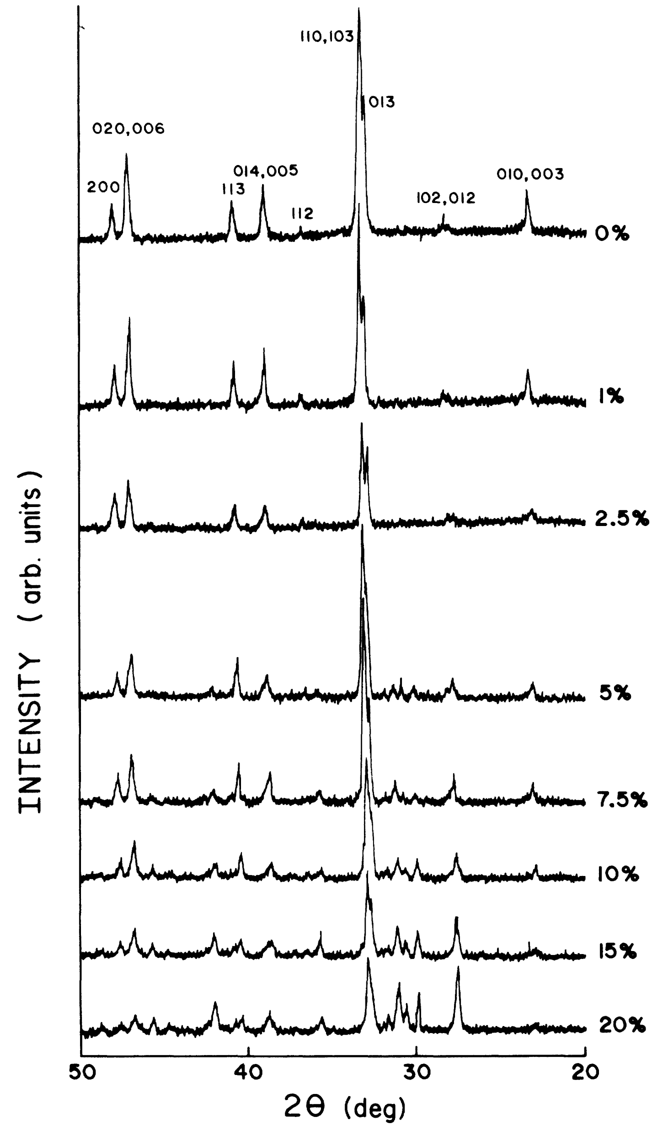

FIG. 3. X-ray-diffraction diagrams of $YBa_2(Cu_{1-x}Mn_x)_3$-$O_{7-\delta}$.

The changes in intensity and peak positions for three other regions of the diffractogram were studied in detail and are shown in Fig. 4. In Fig. 4(a), a detailed analysis of the (006), (020), and (200) reflections shows small

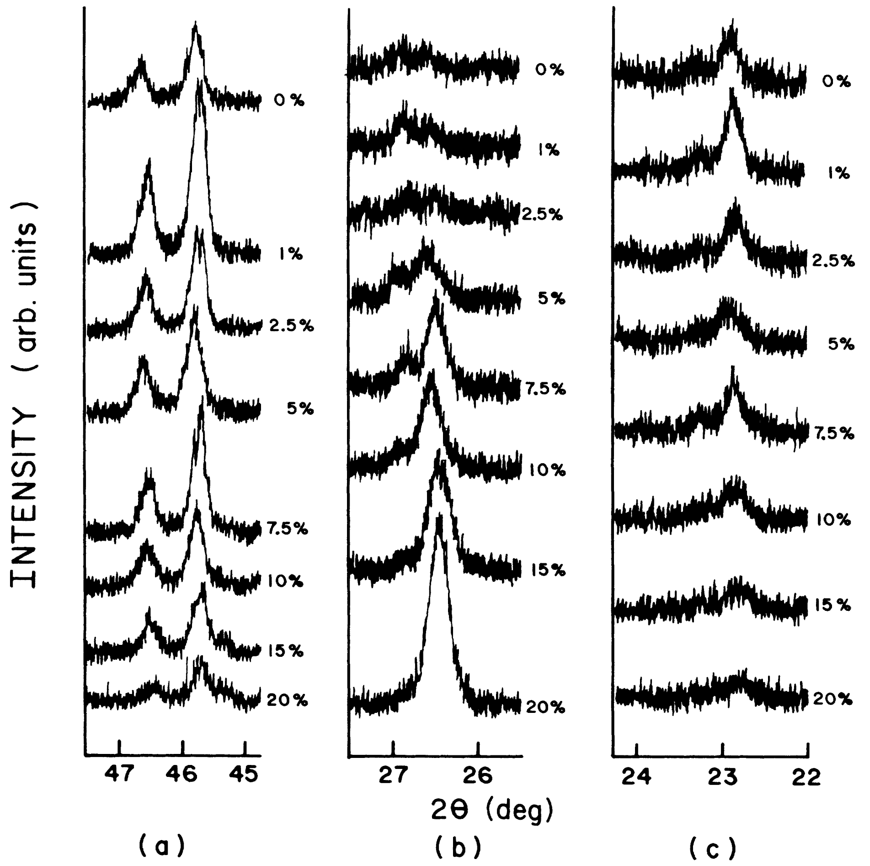

FIG. 4. Three regions of the diffractograms for all Mn concentrations in $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$.

changes in the peak positions throughout all the Mn content. We can note changes in the intensities that first produce a marked splitting in the (006) and (020) peaks, and starting with the sample $x=0.05$, a reversal of the loss of peak definition and broadening of the intensities. For larger x, there is a loss of peak definition and broadening of the reflections. There is a slight change in the (200) and (020) spacings although this cannot be interpreted as a significant modification in the orthorhombic unit cell. This observation is in agreement with the work of Xiao *et al.*[17] In Fig. 4(b), the (102) and (012) peaks seem to fuse to a single, quite intense reflection. The final peak position for this reflection is not the same as that of the (102) reflection of the $YBa_2Cu_3O_{6.5}$ tetragonal phase. Nevertheless, the evolution of the (102) and (012) reflections as a function of the Mn content resembles the changes observed in deoxygenation experiments of the 1:2:3 compound, in which the phase transition from orthorhombic to tetragonal is observed.[19] In Fig. 4(c), a marked loss in the intensity of the (010) and (003) reflections is shown but there is little change in the peak position which may indicate almost no change in the c dimension of the unit cell.

In view of the above observations, one could conclude that Mn introduction in the crystal lattice of $YBa_2Cu_3O_{7-\delta}$ does not produce a sensible modification of the lattice parameters. This was also noted by Xiao *et al.*[17] for $x=0.10$ only. The intensity changes may arise from modifications in the structure factors of the reflections analyzed in this work; the combined changes in peak position and intensity, as in the case of the fusion of the (102) and (012) peaks, may also be due to the change in oxygen occupation of the sites surrounding the Mn ion that substitutes Cu in the Cu positions. Given the moderate influence of the Mn content on T_{onset} suppression, one could indicate the Cu(2) sites in the Cu-O planes as the ones preferentially occupied by the Mn ion. On the other hand, the changes in x-ray spectra described above may well be due to a loss in the oxygen vacancy order, which could indicate that the Mn ion might also occupy the Cu(1) sites in the Cu-O chains. Simulation calculations are underway in an attempt to identify the Mn ion positions in the 1:2:3 compound lattice that will reproduce the experimental observations.

The observations that (1) the superconducting transition width starts broadening around $x=0.10$, and (2) the appearance of additional intragrain phases around $x=0.05$, led us to the idea that Mn can have a solubility limit in the 1:2:3 matrix between $x=0.05$ and $x=0.10$. So, when the substitution exceeds this limit, other phases must precipitate in the matrix in an increasing rate proportional to x. This could lead to transition broadening through an increased inhomogeneity of the sample, which strongly affects the superconducting properties because of the very small coherence length of the high-T_c oxides. Work is in progress for a clear determination of the solubility limit.

In conclusion, we have performed Mn substitution for Cu up to $x=0.20$ in the high-T_c superconductor $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$. Electrical resistivity and magnetic susceptibility measurements showed that the onset of the normal-superconducting transition is little affected by the Mn content. X-ray analysis revealed that the amount of intragrain additional phases increases proportionally to the Mn content. This fact is confirmed by metallographic analysis and resistivity measurements in the normal state. An accurate analysis of x-ray data shows that the 1:2:3 orthorhombic structure is preserved for all the samples, but shows modifications indicative of Mn substitution for Cu.

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