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Journal of Alloys and Compounds 223 (1995) 56–59

Journal of ALLOYS AND COMPOUNDS

Magnetic studies on Mn-substituted Y–Ba–Cu–O

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Received 22 April 1994; in final form 19 September 1994

Abstract

Magnetic d.c. and a.c. susceptibility and lattice constant measurements were performed in the normal state of $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ with Mn concentrations $x=0.075$, 0.15, 0.2, 0.25 and 0.3. The orthorhombic structure is preserved throughout the substitution range and some amount of impurity phases were evidenced in the samples with $x>0.2$. The inter- and intragrain properties from a.c. susceptibility measurements show different behaviour above and below the $x=0.2$ Mn in the YBCO. The measurements of the d.c. susceptibility were analysed using a Curie–Weiss law with a temperature-independent background. The effective magnetic moment obtained per Mn atom, $p_{Mn}=3.29\mu_B$, suggests the presence of a 4+ oxidation state. The variation of the Curie paramagnetic temperature θ for different x is associated with an antiferromagnetic exchange interaction between the Mn ions. A regular trend of $p^2_{eff,tot}$ and T_c as a function of x suggest that below $x=0.2$ Mn ions are substituted in the Cu(1) positions.

Keywords: Superconductors; Magnetic susceptibility; X-ray diffraction

1. Introduction

The behaviour of $YBa_2Cu_3O_7$ under Cu site doping varies considerably since there are two non-equivalent Cu sites Cu(1) and Cu(2) on which a substituent may reside. Relatively little attention has been paid to the substitution of Mn and other lighter 3d transition metals ions because of their small solubility in the structure. It is reported from neutron diffraction and EXAFS work that Mn prefers the Cu(1) site [1–3]. ESR and Raman spectra [4] show that the content of Mn ions in the CuO_2 plane is saturated when x is increased above 0.05 in $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$.

Thermogravimetric analysis gives indirect evidence that Mn substitutes for Cu at the Cu(2) site [5]. Jardim et al. [6–7] found that the substitution of Cu by Mn preserves the orthorhombic structure and leads to a minute diminution of T_c up to $x=0.3$, and that the solubility limit of Mn in the "123" structure is near 0.075. The amounts of extra phases, Y_2BaCuO_5 and the tetragonal $Ba_2Mn_3O_8$ increase with x [7]. Some of the questions regarding normal state properties still remain unanswered.

In this work we present a study of the a.c. and d.c. susceptibility in the $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ superconductor as a function of the Mn content.

2. Experimental

The samples were prepared from mixtures of Y_2O_3, $BaCO_3$, CuO and MnO powders by the solid phases reaction method. The starting materials with a ratio $Y:Ba:Cu:Mn=1:2:(3-x):x$ were mixed in an agate mortar, annealed in air at 900 °C, maintained at this temperature for 48 h, and slowly cooled down to 300 °C. The black powders obtained were pressed into pellets and calcinated at 900 °C for 24 h. The samples were crushed again, annealed in flowing air at 920 °C for 24 h and cooled to room temperature at a rate of 40 °C h^{-1}. The reground samples were pressed into pellets and sintered at 950 °C for 12 h in oxygen atmosphere, following a slow cooling, 30 °C h^{-1}, to 100 °C. In order to obtain good homogeneity, the sintering procedure was repeated at least twice.

SSDI 0925-8388(94)01424-8

The X-ray diffraction patterns were obtained using DRON 2 equipment.

The magnetic susceptibilities were measured with a Faraday-type magnetic balance under a magnetic field of 0.75 T in the temperature range of 80–100 K. The a.c. susceptibility measurements were performed with an a.c. susceptibility bridge operating at a frequency of 666.7 Hz and $H_{a.c.}=0.4$ A m^{-1}.

3. Results and discussion

The X-ray diffraction patterns showed that for Mn concentrations larger than $x=0.2$ impurity phases are present in the samples (Fig. 1), as reported by others [2,7,8]. The measured lattice parameters are $a=3.83$ Å, $b=3.88$ Å, $c=11.68$ Å for all samples with an estimated ± 0.01 Å precision. The values obtained are comparable with the previously reported ones [9].

It has been found from neutron diffraction [1,2] and EXAFS measurements [3] that the Mn ions occupy the Cu(1) chain sites in the "123" lattice and create chain oxygen disorder in the structure.

In order to discriminate between intra- and intergrain properties, a.c. susceptibility measurements were performed. The temperature dependencies of the a.c. susceptibility components χ' and χ'' in the samples with $0 \leqslant x \leqslant 0.3$ are presented in Fig. 2.

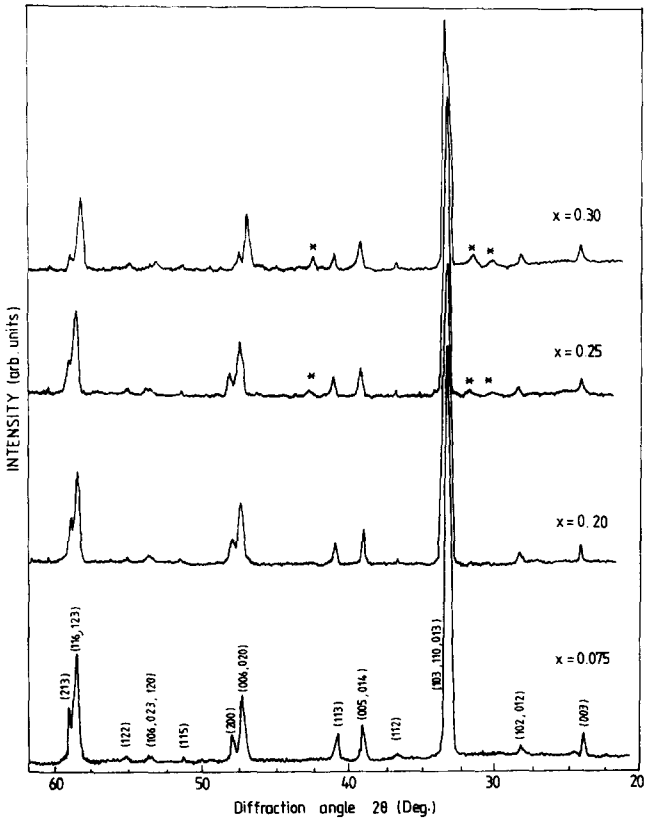

Fig. 1. X-ray diffraction diagrams of $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ samples.

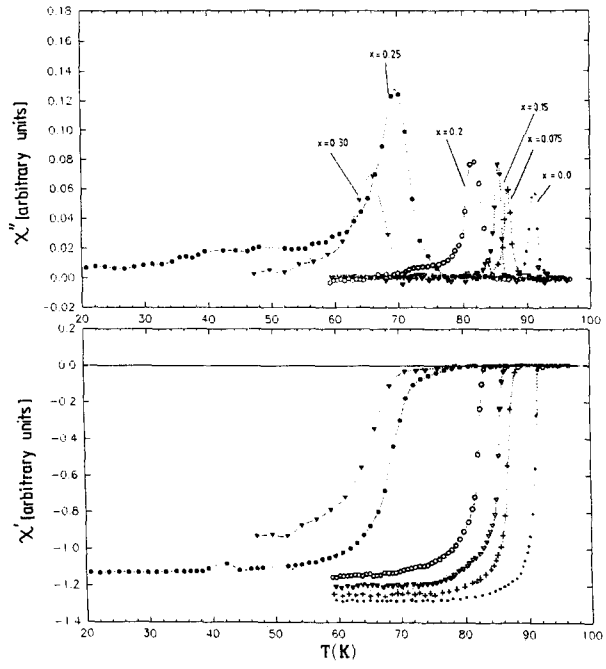

Fig. 2. The a.c. susceptibility of $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ plotted against temperature.

Table 1
The Curie parameters C, θ and the critical transition temperatures in the $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ granular system

x	C (10^{-5} e.m.u. g^{-1} K)	T_{cG} (K)	T_g (K)	ΔT_c (K)	θ (K)
0.075	20.5	88	87.0	1.0	−86
0.15	33.3	86	85.0	1.0	−88
0.20	42.9	83	81.5	1.5	−91
0.25	51.3	78	69.5	7.5	−100
0.30	58.0	77	66.0	11.0	−128

Here we can find several typical features with increasing Mn concentration. First, in the samples with $x \leqslant 0.2$ the diamagnetic signal χ' shows a sharp transition in a single step and the imaginary peak in the $\chi''(T)$ curve is sharp. Secondly, in the concentration range $x>0.2$, the $\chi''(T)$ peak increases and becomes broader, i.e. the $\chi'(T)$ curve shows two distinct steps associated with the weak intergranular coupling. From the χ' plots it is evident that the superconductivity fraction is affected differently by Mn concentration situated above and below $x=0.2$. The intragrain critical temperature T_{cG} and the temperature T_g at which the $\chi''(T)$ peaks are centred starts to decrease with increasing x (Table 1). The T_g values coincide with the temperatures T_{cJ} at which the inflection points in the $\chi'(T)$ curves appear. The temperatures T_{cG} and T_g coincide approximately with the midpoint critical temperatures T_c and the zero resistance temperature from our electrical resistivity

measurements [10]. These temperatures and the transition widths $\Delta T_c = T_{cG} - T_g$ are presented in Table 1.

In the low substitution range ($x \leqslant 0.2$) the sharp peak in χ'' and the small value of $\Delta T_c \simeq 1$ K suggest a good percolation through the weak links between the grains. The weak decrease of the superconductivity fraction for $x > 0.2$ Mn concentration is probably related to the small amount of impurity phases evidenced in the samples (Fig. 1).

The broadening of the ΔT_c width transition and the evolution of $\chi''(T)$ peak shape in the samples with $x > 0.2$ indicate a change in the microstructure of the material, as observed by Jardim et al. [7] and Saini et al. [9].

The analysis of χ' and χ'' data as functions of x clearly indicates the presence of two regions situated below and above $x \simeq 0.2$ in which the inter- and intragrain properties vary in a different way. This fact is evident from the concentration dependence of $T_c = T_{cG}$.

As one can see from Fig. 5 the critical transition temperature T_c smoothly decreases with a rate $dT_c/dx = 0.14$ K/Mn% in the concentration range $0 < x < 0.2$ (assuming a linear dependence of T_c as a function of x). Above $x = 0.2$ the experimental T_c values clearly deviate below the fitted straight line.

The d.c. susceptibility measurements were performed in order to characterize the oxidation state of the Mn ions. Fig. 3 shows the temperature dependence of the susceptibility for $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ samples in the normal state. The susceptibility for the undoped sample ($x = 0$) is temperature-independent and has the value $\chi_0 = 5.1 \times 10^{-7}$ e.m.u. g^{-1}. Fig. 4 shows the inverse susceptibility $[\chi(T) - \chi_0]^{-1}$ plotted against temperature for the samples with $0 \leqslant x \leqslant 0.3$. A Curie–Weiss component is observed in the temperature region above

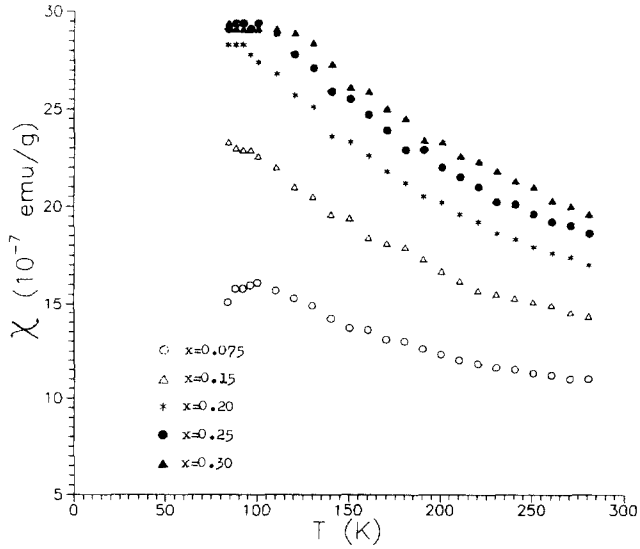

Fig. 3. Temperature dependence of the magnetic susceptibility of $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ superconductor.

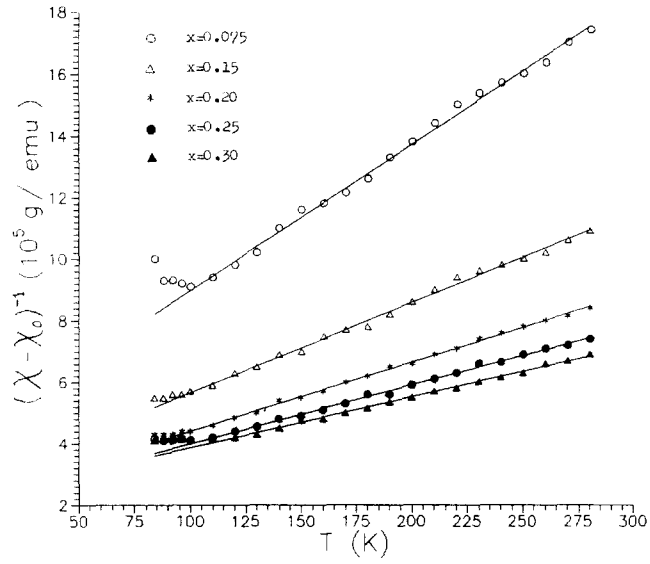

Fig. 4. The inverse of the magnetic susceptibility $[\chi(T) - \chi_0]^{-1}$ as a function of temperature for the $YBa_2Cu_{3-x}Mn_xO_{7-\delta}$ superconductor.

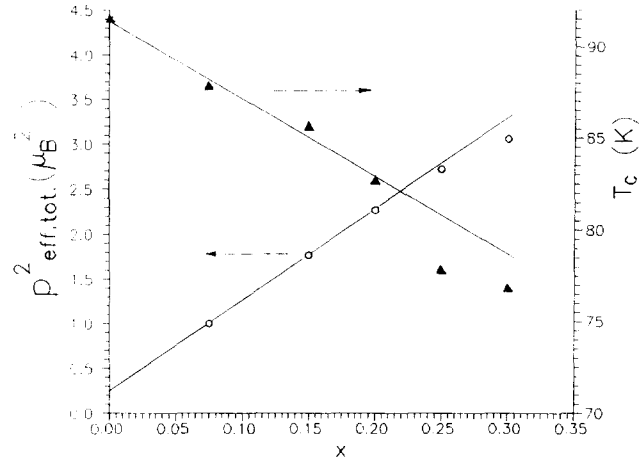

Fig. 5. The square of the total magnetic moment $p_{eff.tot}^2$ and the critical temperature T_c as a function of Mn concentration.

100 K. This type of behaviour may be attributed to the local moment of Mn ions. The temperature dependence of the susceptibility (Fig. 3) can be written as the sum of the temperature-independent susceptibility, χ_0, and a Curie–Weiss term as follows:

$$\chi(T) = \chi_0 + \frac{C}{T - \theta} \tag{1}$$

where C is the Curie constant and θ the paramagnetic temperature. A fit of our experimental data according to Eq. (1) yields the parameters C and θ given in Table 1. As one can see, θ increases with increasing x, to reach a value of $\theta = -128$ K for $x = 0.3$.

From the Curie constant C we obtained the effective total magnetic moment $p_{eff.tot}$ per unit cell. The square of this magnetic moment increases almost linearly up to $x = 0.2$ as shown in Fig. 5. For $x > 0.2$ the dependence

of $p_{\text{eff.tot}}^2$ deviates from linearity. Assuming that the Mn ions substitute only on the chain sites, we have in the region of linear dependence:

$$Np_{\text{eff.tot}}^2 = N_{\text{Cu}}p_{\text{Cu}}^2 + N_{\text{Mn}}p_{\text{Mn}}^2 \quad (2)$$

In the following, we consider that the $p_{\text{eff.tot}}$ contains two contributions: one due to the Mn atoms, μ_{Mn}, which is concentration-dependent, and a constant μ_{Cu}, due to the paramagnetic Cu^{2+} ions [11,12]. Taking into account that the Mn ions substituted only in the chain sites and that the constant contributions in $p_{\text{eff.tot}}$ arise from both Cu(1) and Cu(2) sites, Eq. (2) becomes:

$$p_{\text{eff.tot}}^2 = 3p_{\text{Cu}}^2 + x(p_{\text{Mn}}^2 - p_{\text{Cu}}^2) \quad (3)$$

The fit of the experimental data points, Fig. 5, with Eq. (3) gives $p_{\text{Cu}} = 0.32\mu_{\text{B}}$ and $p_{\text{Mn}} = 3.29\mu_{\text{B}}$. The value of p_{Cu} mentioned above is smaller than that $0.48\mu_{\text{B}}$ reported in Fe:YBaCO for example [12]. We cannot yet discern whether this difference is simply due to different kinds of sample or to some other reasons.

The value of $3.29\mu_{\text{B}}$ obtained for the p_{Mn} suggests the presence of an 4+ oxidation state for the Mn ions. The value agrees with the $p_{\text{Mn}} = 2[S(S+1)]^{1/2} = 3.87\mu_{\text{B}}$ calculated for the Mn^{4+} free ion. This oxidation state in Mn ions in YBCO has been already proposed from titration measurements [2,9,13].

The smooth increase of $p_{\text{eff.tot}}^2$ with a rate of $0.034\mu_{\text{B}}^2$/%Mn and the afferent decrease of the critical transition temperature with $dT_c/dx\% = 0.4$ K/%Mn agree well with the assumption that the small fraction of dissolved Mn ions ($\leqslant 0.2$) possibly occupies the Cu(1) sites. Additionally, the negative values of the paramagnetic Curie temperature $\theta \simeq -86$ °C, -90 °C suggest an antiferromagnetic exchange interaction between the Mn^{2+} ions occupying various neighbouring Cu(1) sites. The chain disorder created in the structure by these Mn ions, does not affect much the density of states in the Cu(2)O layers and T_c smoothly decreases. When the Mn concentration is above $x = 0.2$, the excess of the dopant drains out of the superconductivity matrix into the impurity phases, in which the AF interaction between the Mn ion increases ($\theta = -128$ °C, e.g. in the sample with $x = 0.3$).

4. Conclusions

The solubility of the Mn ions in Y–Ba–Cu–O is limited at $x \simeq 0.2$ and the basic orthorhombic structure is preserved for all samples.

The smooth decrease of the intragrain critical temperature $T_{cG} = T_c$ and the weak decrease of the superconducting fraction with increasing x up to 0.2, agree with the assumption that Cu(1) is substituted by Mn. The small value of the transition width and the sharp peak in $\chi''(T)$ suggest a small influence of the Mn ions on the intergrain properties in the samples with $x \leqslant 0.2$.

The temperature dependence of magnetic susceptibility in the normal state shows a Curie–Weiss component above 100 K. Assuming that Cu ions are substituted by Mn, the presence of an oxidation state 4+ for manganese ions and an antiferromagnetic exchange between them is obtained by fitting the experimental data. The regular trend of the square of the total magnetic moment $p_{\text{eff.tot}}^2$ and of the critical transition temperature as a function of x is evident below the $x = 0.2$ concentration of Mn in the 123 lattice. The deviation from linearity of $p_{\text{eff.tot}}^2(x)$ in the substitution range $x > 0.2$ and the change in the inter- and intragrain properties are related to the impurity phases positively evidenced by XRD.

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