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## Linear $T_c$ depression in Mg-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We report resistivity-versus-temperature measurements performed on polycrystalline pellets of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  made using the polymer-metal-complex precursor method.  $T_c$  was found to decrease linearly with increasing Mg doping in the range  $x = 8.6 \times 10^{-4}$  to  $8.6 \times 10^{-3}$  with slope  $-1400$  K/ $x$ ; the normal-state resistivity and the superconducting transition width showed little or no change. Mg was found to have a maximum solubility in  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  of  $x \approx 9 \times 10^{-3}$ .

Studies of the metal ( $M$ ) substituted compound  $\text{YBa}_2(\text{Cu}_{1-x}M_x)_3\text{O}_{7-\delta}$  with  $M = \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Ga}$ , and  $\text{Al}$  have been performed by a number of groups<sup>1-4</sup> with  $x$  ranging from 0.01 to an upper limit of  $\sim 0.1$  for most of these elements and as high as  $x = 1$  for Fe and Co. These studies have shown the important role of Cu in the superconductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Y-Ba-Cu-O). Xiao *et al.*<sup>2</sup> and Tarascon *et al.*<sup>3</sup> have pointed out the importance of the valence state of the substituting metal  $M$  and the different effects of substitutions at the two distinct Y-Ba-Cu-O copper sites in promoting structural and superconducting changes in Y-Ba-Cu-O. The effect on  $T_c$  of a given substitution depends on the substituted element's valence state and relative concentration with respect to Cu. For a divalent element such as Zn,  $T_c$  drops linearly with Zn concentration up to a solubility limit in Y-Ba-Cu-O of  $x \approx 0.1$ .<sup>2,3</sup> Trivalent elements such as Co and Fe have little effect on  $T_c$  for  $x < 0.05$  and cause  $T_c$  to drop at higher concentrations.<sup>3</sup> We report here a systematic study of Mg for Cu substitutions in the range  $8.6 \times 10^{-4} \leq x \leq 8.6 \times 10^{-3}$ . Previous divalent Cu substitutions have been performed at higher doping levels with 3d transition metals having substantially different electronic configurations from Mg.<sup>1-4</sup>

Samples were made using the polymer-metal-complex precursor technique.<sup>5,6</sup> This method involves dissolving the constituent elements in a solution after which the dissolved ions bind to polymers and form a polymer-metal complex. After formation of the polymer-metal complex, the solvent is evaporated and a series of heat treatments eliminates the polymer and causes the constituent elements to react forming Y-Ba-Cu-O. For samples in this study, the Y-Ba-Cu-O reaction occurred during a heat treatment at 940°C for 2 h in flowing  $\text{O}_2$ . The resulting material was then ground and pressed into pellets and given an additional heat treatment at 940°C for 2 h in flowing  $\text{O}_2$ . As a result of dissolving Y, Ba, and Cu ions in solution and the formation of a polymer-metal complex, these elements are mixed on an atomic level before

the Y-Ba-Cu-O forming reaction. The Mg doping was achieved at the solution stage by dissolving  $\text{Mg}(\text{NO}_3)_2$  in water, which was added to a solution of Y, Ba, and Cu nitrates in dimethylformamide to give the desired ratio of Mg:Cu. Two separate series of samples were made, one in which Cu was not decreased with Mg doping and having nominal composition  $\text{YBa}_2(\text{Cu}_1\text{Mg}_x)_3\text{O}_{7-\delta}$  with  $x$  varying from  $2 \times 10^{-4}$  to 0.2 and one in which the amount of Cu was reduced commensurate with the level of Mg doping so as to give a nominal composition  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  with  $x$  varying from  $8.6 \times 10^{-4}$  to 0.022. We did not determine the actual composition of the realized compounds.

Powder x-ray diffractograms of selected samples were obtained using a Siemens D-500 diffractometer for a batch of  $\text{YBa}_2(\text{Cu}_1\text{Mg}_x)_3\text{O}_{7-\delta}$  samples with nominal  $x$  values in the range  $4 \times 10^{-4} \leq x \leq 0.02$ . These showed no detectable change in lattice parameters with  $x$  within our resolution of 0.03 Å.

Resistance measurements were made using a DC reversing-current technique at current densities from 0.4 to 0.9 A/cm<sup>2</sup> with the sample mounted in a four-lead configuration. Resistivity was calculated from measurements of the sample cross-sectional area and the distance between voltage contacts and has an estimated uncertainty of approximately  $\pm 10\%$ ; the uncertainty is primarily due to uncertainty in the measurement of the area. We have also found the resistivity to be sensitive to variations in sample density. As a result, we believe that modest room-temperature resistivity variations between samples of 20% are not significant. Samples were enclosed in a <sup>4</sup>He exchange gas cryostat and the sample resistance,  $R(T)$  was measured continuously as the cryostat was slowly cooled. A typical cooling rate near  $T_c$  was  $dT/dt \approx 0.2$  K/min.

The two series of Y-Ba-Cu-O-Mg pellets showed similar behavior. For Mg concentrations less than  $x \approx 0.01$ ,  $T_c$  dropped linearly with increasing Mg concentration and the normal-state resistivity showed no significant

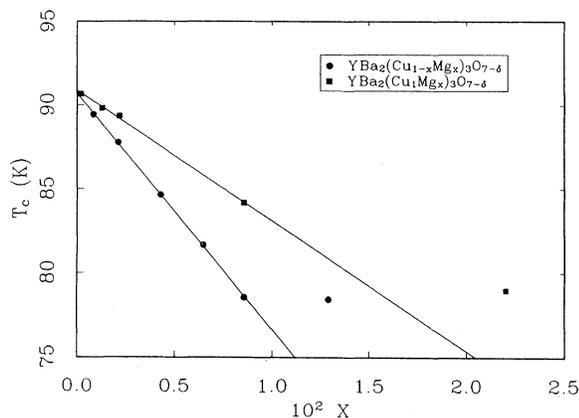


FIG. 1.  $T_c$  vs nominal  $x$  for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  and  $\text{YBa}_2(\text{Cu}_1\text{Mg}_x)_3\text{O}_{7-\delta}$  samples.

change with  $x$ . Plots of  $T_c$  versus  $x$  are shown in Fig. 1 for the two series of samples. For convenience,  $T_c$  was taken as the point in the superconducting transition at which the resistance had fallen to  $\frac{1}{2}$  of its normal-state value at  $T \gtrsim T_c$ . Figure 1 shows that both series of samples have a linear drop in  $T_c$  with increasing  $x$ , the nominal  $\text{YBa}_2(\text{Cu}_1\text{Mg}_x)_3\text{O}_{7-\delta}$  samples have slope  $-780 \text{ K}/x$  and the nominal  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  samples have slope  $-1400 \text{ K}/x$ . The  $dT_c/dx$  of  $-1400 \text{ K}/x$  is comparable to the value of  $-1300 \text{ K}/x$  reported by Xiao *et al.*<sup>2</sup> for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$ . Both series of samples show a leveling off of  $T_c$  at 78 K. We interpret the leveling off of  $T_c$  as due to Mg solubility limits of  $x_a \approx 9 \times 10^{-3}$  for nominal  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  and  $x_b \approx 1.5 \times 10^{-2}$  for nominal  $\text{YBa}_2(\text{Cu}_1\text{Mg}_x)_3\text{O}_{7-\delta}$ .

For nominal concentrations greater than  $x_a$  and  $x_b$ , respectively, the  $T_c$  stabilized, the superconducting transition region broadened, and the normal-state resistivity increased. Figure 2 shows  $\rho(T)$  plots from 75 to 95 K for the  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  samples for which  $T_c(x)$  is plotted in Fig. 1. The broadening of the transition and the increase in normal-state resistivity are characteristic of Y-Ba-Cu-O samples we have made previously which contained impurity phases. We believe that this behavior in these Y-Ba-Cu-O-Mg samples results from impurity phases that occur above  $x_a \approx 9 \times 10^{-3}$ , consistent with a Mg solubility limit of  $x \approx 9 \times 10^{-3}$  for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$ .

Because of the apparent low-solubility limit of Mg in Y-Ba-Cu-O, it is difficult to verify directly that Mg is substituting for Cu. Another possibility is that Mg may substitute for its fellow group IIa element Ba. We believe that Mg substitutes for Cu for two reasons. The ionic radius of divalent Mg is 0.69 Å which is quite close to the value of 0.72 Å for divalent Cu. Divalent Ba, on the other hand, has an ionic radius of 1.34 Å. The absence of a change in lattice parameters with  $x$  suggests that Mg is substituting for Cu rather than Ba. Also, the similarity

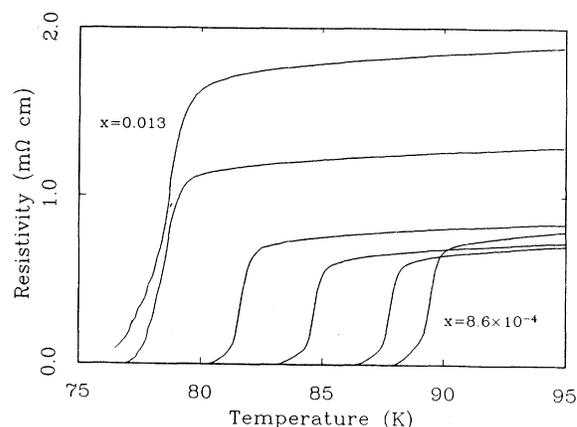


FIG. 2. Resistivity vs temperature of the  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  samples for which  $T_c$  is plotted in Fig. 1. These samples have nominal  $x$  values of  $1.3 \times 10^{-2}$ ,  $8.6 \times 10^{-3}$ ,  $6.45 \times 10^{-3}$ ,  $4.3 \times 10^{-3}$ ,  $2.2 \times 10^{-3}$ , and  $8.6 \times 10^{-4}$ .

in  $dT_c/dx$  seen between our  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  samples and that reported by Xiao *et al.*<sup>2</sup> for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-\delta}$  samples suggests that Mg substitutes for Cu.

A surprising aspect of the data shown in Fig. 1 is the nearly factor of 2 difference in slope between the two series of samples for differences in nominal Cu content (i.e.,  $\text{Cu}_x$  versus  $\text{Cu}_{1-x}$ ). These differences in Cu content range from  $\sim 0.1\%$  for the lowest Mg-doping levels to a maximum of  $\sim 1\%$  near the Mg solubility limit. Our synthesis method enables control of nominal Mg content to 0.01x or better, so the difference is not due to a systematic error in nominal  $x$ . Since the different samples were given identical heat treatments, we do not believe that the difference in slope is due to differences in processing. A possible explanation for the discrepancy in slopes is that, for the nominal  $\text{YBa}_2(\text{Cu}_1\text{Mg}_x)_3\text{O}_{7-\delta}$  samples, the realized value of  $x$  may be less than the nominal value due to excess Cu in these samples.

Based on the preceding evidence, we believe that Mg substitutes for Cu in all of our samples and, accordingly, the composition of the realized compound is actually  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  regardless of the nominal composition.

It is not surprising that Mg and Zn have very different solubility limits in Y-Ba-Cu-O considering their different electronic configurations. Given the large difference in solubility limits and different electronic configurations of these two elements, it is surprising that they appear to have similar effects on  $T_c$ . It has been proposed that conduction in Y-Ba-Cu-O occurs as the result of hybridization between Cu 3d and O 2p orbitals.<sup>7</sup> Given this, it is reasonable to expect that the substitution of Mg, which has no 3d electrons, should have a larger effect on  $T_c$  than Zn, which has a similar electronic structure to Cu. It appears that this is not the case.

In conclusion, we have performed a systematic

study of the effect of Mg doping on  $T_c$  for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Mg}_x)_3\text{O}_{7-\delta}$  in the concentration range  $8.6 \times 10^{-4} \leq x \leq 8.6 \times 10^{-3}$ . Our results suggest that the effect of these substitutions on  $T_c$  is comparable to what others have observed for Zn, although the solubility limit of Mg is apparently quite different than that of Zn.

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- <sup>1</sup>Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshini, A. Minami, and T. Fujita, *Nature* **328**, 512 (1987).  
<sup>2</sup>G. Xiao, M. Z. Cieplak, A. Gavrin, F. H. Streitz, A. Bakhshai, and C. L. Chien, *Phys. Rev. Lett.* **60**, 1446 (1988).  
<sup>3</sup>J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, and S. A. Sunshine, *Phys. Rev. B* **37**, 7458 (1988).  
<sup>4</sup>M. Mehbod, W. Biberacher, A. G. M. Jansen, P. Wyder, R.

- Deltour, and P. H. Duvigneaud, *Phys. Rev. B* **38**, 11 813 (1988).  
<sup>5</sup>J. C. W. Chien, B. M. Gong, J. M. Madsen, and R. B. Hallock, *Phys. Rev. B* **38**, 11 853 (1988).  
<sup>6</sup>J. C. W. Chien, B. M. Gong, X. Mu, and Y. S. Yang, *J. Polymer Sci. A* **28**, 1999 (1990).  
<sup>7</sup>W. E. Pickett, *Rev. Mod. Phys.* **61**, 433 (1989).