

## Anomalously large $T_c$ depression by Zn substitution in Y-Ba-Cu-O

B. Jayaram, S. K. Agarwal, C. V. Narasimha Rao, and A. V. Narlikar  
*National Physical Laboratory, Hillside Road, New Delhi 110012, India*

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A systematic study of  $T_c$  variation on Zn substitution for Cu in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  is reported.  $T_c$  decreases linearly from 89 K to the nonsuperconducting state at an unusually large rate of over 15 K/at.% of substitution. Over the entire concentration range no orthorhombic-to-tetragonal change is observed. The  $T_c$  depression and the negative  $dR/dT$  found for higher Zn concentration have been attributed to some of the unique characteristics of Zn.

The most unusual characteristic of the oxygen-deficient perovskite Y-Ba-Cu-O superconductors is the fact that their change in  $T_c$  with respect to the substitution is site dependent. In the case of the majority of rare-earth substitutions, which occur on the Y site of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  (henceforth to be referred as the 1-2-3 compound),  $T_c$  is only marginally affected.<sup>1</sup> On the other hand,  $3d$  magnetic elements in this compound occupy Cu sites and are found to depress  $T_c$  considerably,<sup>2,3</sup> though the effect is nowhere as pronounced as in the majority of conventional superconductors. Interestingly, some nonmagnetic ions such as Al (Ref. 4) and Ga (Ref. 5), which also occupy Cu sites, when incorporated beyond a certain small threshold concentration, are found to depress  $T_c$  quite effectively. This has been attributed to the orthorhombic-to-tetragonal (O-T) transformation, accompanied by a change in the oxygen stoichiometry. Amongst these substitutions, as revealed by Tarascon *et al.*<sup>6</sup> on the 2-1-4 compound and by others on 1-2-3 systems of Y (Refs. 7-9) and Eu (Ref. 10), no case is perhaps as intriguing as that of Zn, where the reported  $T_c$  depression is most pronounced. In this paper, we report systematic studies on Zn substitution in the yttrium-based 1-2-3 compound which confirms that (i) the  $T_c$  depression is several times greater than reported for any of the magnetic or nonmagnetic substitutions at Cu sites, (ii) the decrease in  $T_c$ , almost up to complete suppression of superconductivity, is linear with Zn concentration, and (iii) there is no discernible change in the crystal structure. The results are discussed in terms of some of the unique features associated with Zn, such as its fixed valency, filled  $d$  shell, and preference for octahedral coordination. These aspects reduce the carrier concentration and cause Zn to occupy Cu chain sites preferentially.

Samples of the  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{7-y}$  system with  $0.0 \leq x \leq 0.1$  were prepared by solid-state reaction of the constituent oxides. X-ray diffraction spectra revealed the presence of a single phase. The line positions were identical with that of the 1-2-3 compound, which confirms that the lattice parameters remained invariant with Zn substitution. Also, in this concentration range of Zn substitution, the x-ray data gave no indication of a gradual decrease in orthorhombicity of the unit cell. This agrees with the contentions of Maeno *et al.*<sup>2</sup> and Strobel, Paulsen, and Tholence,<sup>7</sup> who found that, for samples with Zn concentration of  $x=0.033$  and  $0.041$ , the structure

remained orthorhombic. From the closeness of the ionic radius of Zn (0.74 Å) to that of Cu (0.72 Å) and from the absence of any second phase, it seems reasonable to conclude that Zn substitutes for Cu in the 1-2-3 compound. Also, as the Zn concentration in all these samples is rather small, it is not surprising that the present x-ray diffraction studies have not indicated any noticeable change in the lattice parameters.

The dc resistance of the samples is measured over the temperature range of 4-130 K by a conventional four-probe technique. Figure 1 depicts the temperature dependence of the resistance. The variation in the absolute values of the resistivity for different samples is not presented as the experiments were performed on disk-shaped samples of varying thickness. The transition width is found to increase from 2 K for  $x=0$  to 17 K for  $x=0.057$ . The last sample showed  $R=0$  at 3 K. For low concentrations of Zn, the variation of resistance with temperature is metallic, but in the vicinity of  $x=0.033$  it tends to become flat and for higher concentrations of Zn the resistance shows negative  $dR/dT$ .

Figure 2 shows  $T_c(R=0)$  plotted as a function of Zn concentration. It is interesting to note that  $T_c$  decreases linearly from 89 to 3 K with  $x$ . This is in contrast to the cases of Al (Ref. 4) and Fe (Ref. 11), which show two distinct slopes, which in Al is attributed to the orthorhombic-to-tetragonal phase change and in Fe to the formation of an additional magnetic phase. The  $T_c$  depression obtained from the initial slopes in both cases is about 3 K/at.% of Cu substitution, whereas, surprisingly the results presented in Fig. 2 indicate the  $T_c$  depression to be about 15 K/at.% of Zn substitution. Extrapolation of the straight line (Fig. 2) shows the sample with  $x=0.06$  to be nonsuperconducting. For  $x > 0.057$ , the samples showed only a semiconductorlike behavior and did not become superconducting down to the lowest temperature studied.

Generally, the reasons that reduce  $T_c$  are (i) orthorhombic-to-tetragonal transformation, (ii) change in oxygen stoichiometry, (iii) pair breaking due to the magnetic moment of the dopant, (iv) decrease in the Debye temperature  $\Theta_D$ , (v) disordering effect, and (vi) reduction in the carrier concentration leading to a decrease in the density of states  $N(E_F)$ . The present result of  $T_c$  depression due to Zn substitution cannot be ascribed to orthorhombic-to-tetragonal transformation. Since we are substituting divalent Zn in place of divalent Cu, and in

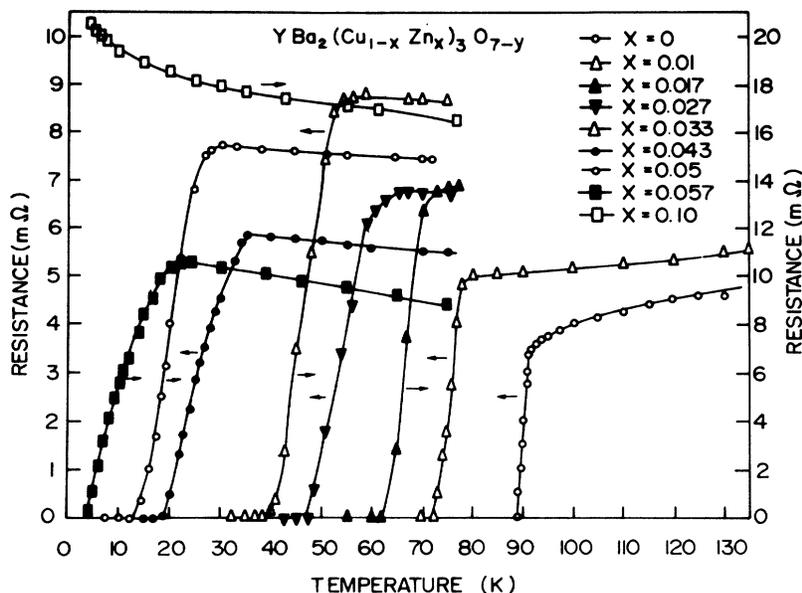


FIG. 1. Resistance vs temperature curves for various Zn-substituted samples.

very small concentrations, any substantial change in the oxygen stoichiometry is not to be expected. If the observed change in  $T_c$  were due to a change in the oxygen stoichiometry one would have expected a steplike decrease<sup>12</sup> in  $T_c$  with  $x$ , instead of the linear depression depicted in Fig. 2. Because of the nonmagnetic nature of Zn, direct pair breaking due to magnetic interaction is unlikely to be the cause of the decrease in  $T_c$ . Also, the Zn concentration is too small to induce a magnetic moment on Cu (Ref. 6) that could be responsible for the depression in  $T_c$ .

The anomalously large decrease in  $T_c$  due to Zn substitution can be attributed to some of the unique characteris-

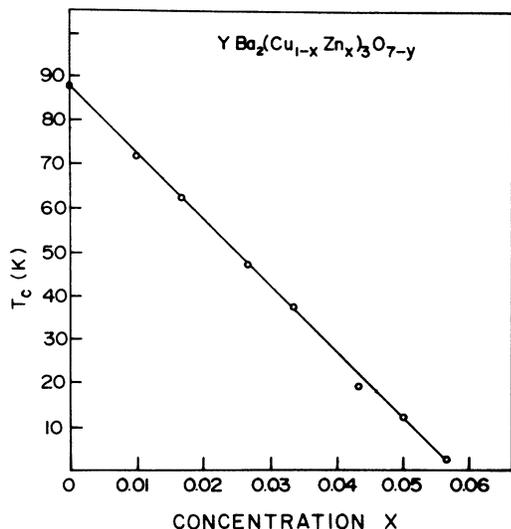


FIG. 2. Variation of  $T_c$  with Zn concentration  $x$  in  $YBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ .

tics of Zn (compared to other substitutions) together with the disordering effect and the impending decrease in the density of charge carriers. Because of the matching of the ionic radii, Zn would substitute for Cu in the 1-2-3 lattice. Owing to the completely filled  $d$  orbital of Zn there is a diminished overlap of Zn  $d$  orbitals with oxygen  $p$  orbitals. Coupled with this, the fixed divalent oxidation state of Zn at Cu sites, in chains or planes, is expected to significantly impair the charge-transfer process and thereby reduce the effective carrier concentration. Hall-effect measurements on 1-2-3 compounds with varying oxygen stoichiometry and possessing various  $T_c$  values have shown that though the carrier concentration decreases only marginally, the  $T_c$  decreases rapidly, with metallic behavior changing to semiconductorlike.<sup>13</sup> Interestingly, since the range of coherence in the  $ab$  plane is approximately 20 Å, a rough estimate suggests that 5-6% of Zn at Cu site is sufficient to disturb the coherence.

Zn as such should substitute for Cu both in chains [Cu(1)] and planes [Cu(2)]. As Zn prefers the octahedral coordination the occupancy of the former sites seems more probable. This would lead to random occupation of Cu(1) sites resulting in filling up of neighboring O(5) sites. This does not necessarily mean the oxygen content per formula unit would go up, as neutron diffraction studies on the pure 1-2-3 compound show that only about 5% of O(5) sites are occupied.<sup>14</sup> However, the chain structure would randomly be disrupted and such a disordering effect is known to reduce  $T_c$ .<sup>12</sup>

The changeover from metallic to semiconductorlike behavior of resistance is gradual with Zn substitution which obviously is not due to the structural transition. This behavior can again be ascribed to the localization effect or to decrease in the carrier concentration. Perhaps the observed increase in the transition width with higher Zn concentration, depicted in Fig. 1, is a manifestation of disorder.

To sum up, the large  $T_c$  decrease with small Zn substitution is attributed to Zn going to Cu(1) and Cu(2) sites in that order of preference and to the unique characteristics of Zn. The latter are expected to bring down the effective carrier concentration and also cause local disorder. Interestingly, the preliminary results obtained on Zn-substituted La-Sr-Cu-O compounds are essentially similar, with  $T_c$  decreasing at the rate of about 10 K/at. %

of substitution. Details of the absolute values of resistivity of Zn-substituted yttrium and lanthanum compounds will be reported elsewhere.

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- <sup>1</sup>P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, *Phys. Rev. Lett.* **58**, 1891 (1987).
- <sup>2</sup>Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, *Nature* **328**, 512 (1987).
- <sup>3</sup>G. Xiao, F. H. Streitz, A. Garvin, Y. W. Du, and C. L. Chien, *Phys. Rev. B* **35**, 8782 (1987).
- <sup>4</sup>T. Siegrist, L. F. Schneemeyer, J. V. Waszczak, N. P. Singh, R. L. Opila, B. Batlogg, L. W. Rupp, and D. W. Murphy, *Phys. Rev. B* **36**, 8365 (1987).
- <sup>5</sup>M. Hiratani, Y. Ito, K. Miyauchi, and T. Kudo, *Jpn. J. Appl. Phys.* **6**, L1997 (1987).
- <sup>6</sup>J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. McInff, Jr., *Phys. Rev. B* **36**, 8393 (1987).
- <sup>7</sup>P. Strobel, C. Paulsen, and J. L. Tholence, *Solid State Commun.* **65**, 585 (1988).
- <sup>8</sup>P. Mandal, A. Poddar, P. Choudhury, A. N. Das, and B. Ghosh, *J. Phys. C* **20**, L953 (1987).
- <sup>9</sup>M. Veit, J. Langen, M. Galfy, H. D. Jostarndt, A. Erle, S. Blumenroder, H. Schmidt, E. Zirngiebl, and G. Guntherodt, in *Proceedings of the International Conference on High Temperature Superconductors: Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, 1988*, edited by J. Muller and J. L. Olsen [Physica C (to be published)].
- <sup>10</sup>H. A. Borges, G. L. Wells, S. W. Cheong, R. S. Kwok, J. D. Thompson, Z. Fisk, J. L. Smith, and S. B. Oseroff, *Physica B* **148**, 411 (1987).
- <sup>11</sup>M. Mehbod, P. Wyder, R. Deltour, Ph. Duvigneaud, and G. Naessens, *Phys. Rev. B* **36**, 8819 (1987).
- <sup>12</sup>R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Nature* **329**, 423 (1987).
- <sup>13</sup>Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, *Phys. Rev. B* **36**, 7222 (1987).
- <sup>14</sup>J. D. Jorgensen (unpublished).