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T_c depression in the $YBa_2Cu_{4-x}M_xO_8$ system for $M=$Fe, Ni, Zn, and Ga

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Observations show that T_c depression of the $YBa_2Cu_4O_8$ system resulting from disorder caused by partial replacement of Cu by metallic dopants Fe, Ni, Zn, and Ga, in small concentrations, is significantly faster than in the $YBa_2Cu_3O_7$ system. Another feature of T_c suppression in the $YBa_2Cu_4O_8$ system is that the effect of Fe and Ni is much stronger in this system than that of Zn. These features are analyzed in terms of the hole occupancy of the doubly charged impurity atoms in two circumstances—first when the impurity is isolated, and the other when it is in the crystal environment. On this basis the observations support a mechanism of T_c suppression wherein the moments of the impurity acquire effectively more isolated-atom-like character in the $YBa_2Cu_4O_8$ system and wherein the pairing interaction is also suppressed directly.

Since their discovery, high-T_c cuprates have been subjected to extensive substitutional studies[1] to investigate how their superconductivity responds to substitutional disorder resulting from incorporation of metallic dopants at different cationic sites of their crystallographic unit cell. Coupled to the inherent interest in the search for a non-copper-based superconducting system of high T_c, much of the efforts have been directed to explore the effects arising from copper-site substitutions. In this respect the $YBa_2Cu_3O_7$ (Y 1:2:3) system, possessing a T_c of about 90 K, has been the target of the most elaborate and extensive studies to determine how T_c changes when either of its two copper sites, namely, the chainer site Cu(1) or the planar site Cu(2), are partially substituted by dopants such as Fe, Ni, Zn, and Ga, which from various chemical considerations are regarded as suitable substituents for Cu. With all these substitutions, in small concentrations up to about 5 at. %, the effect on superconductivity is however deleterious with T_c getting suppressed at a rate of about 5, 3, 15, and 4 K/at. %, respectively, for Fe, Ni, Zn, and Ga.[1] The neutron diffraction backed by Mössbauer studies in the case of Fe confirm that at such small concentrations Fe and Ga prefer the chainer Cu(1) site while Ni and Zn tend to occupy the planar Cu(2) site of Y 1:2:3 structure.[1] On the other hand, differential anomalous x-ray scattering[2] shows that Ni and Zn dopants occupy the Cu(1) and Cu(2) sites randomly. However, the majority of the experiments favor the former possibility.

Essentially similar to the Y 1:2:3 system is the $YBa_2Cu_4O_8$ (Y 1:2:4) system possessing the T_c of about 80 K. The striking difference between the two systems is that while the unit cell of the former contains a single Cu-O chain, that of the latter has two adjacent Cu-O chains. Surprisingly, however, in contrast to Y 1:2:3, there are only limited reports of substitutions in the Y 1:2:4 system. An obvious reason for this is that the latter is, in general, difficult to synthesize in pure single-phase form, which is achieved either by using high-pressure oxygen[3] or a suitable catalyst.[4] Only limited substitutional studies in place of Cu have been reported for the Y 1:2:4 system. Kodama *et al.*[5] have investigated the substitution of Fe and Co and their results indicate that, as with the Y 1:2:3 system, Fe and Co prefer the chainer Cu(1) sites. These results pertaining to Fe are also corroborated through Mössbauer studies of Felner and Brosh[6] and HRTEM observations of Matsui and Yanagisawa.[7] Their results[6] on Zn substitution are consistent with the Y 1:2:3 system, in that Zn prefers the planar Cu(2) site. HRTEM studies on the Ni-doped 1:2:4 system[7] have indicated that Ni may occupy both Cu(1) and Cu(2) sites. Despite the above similarities in the Y 1:2:4 and Y 1:2:3 systems regarding the site occupancy of different dopants, the two systems seem to differ markedly in respect of the effect these dopants have on T_c. Although such copper-site substitutions adversely affect T_c in both the systems, the rate of T_c depression in Y 1:2:4, as reported in the above references, is found to be two to four times more than in the Y 1:2:3 system.

This motivated us to make a systematic study of doping effects on T_c in the $YBa_2Cu_{4-x}M_xO_8$ system for $M=$Fe, Ni, Zn, and Ga. The samples of the Y 1:2:4 series containing up to 3–4 at. % of the above dopants were synthesized by using sodium oxalate as flux and following the processing schedule described earlier.[8] The single-phase nature of these samples was ascertained by x-ray diffraction (XRD).

While a detailed study of the above four series of samples forms a subject matter of a separate communication,[9] the pertinent results relevant for the present paper are depicted here. Figure 1 summarizes T_c suppression data for all four dopants, Fe, Ni, Zn, and Ga, in the Y 1:2:4 system. Their respective rates of T_c decrease are also indicated in Fig. 1.

From Fig. 1 the following features of T_c suppression in the Y 1:2:4 system are clear.

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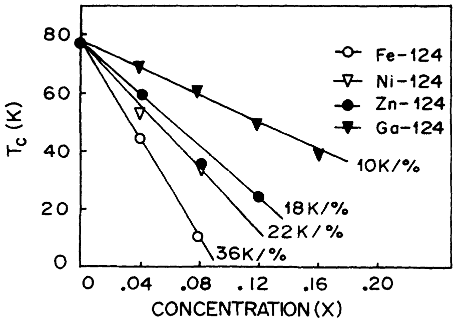

FIG. 1. Degradation of T_c of Y 1:2:4 with doping of Fe, Ni, Zn, and Ga. Their respective rates of T_c suppression are given in the figure.

(1) The rates of T_c depression for Y 1:2:4 are significantly larger than the corresponding rates for the Y 1:2:3 system for all the dopants.

(2) While the effect of Zn is strongest in the Y 1:2:3 system, it is weaker in the Y 1:2:4 system than that of the effects of Fe and Ni. More clearly, the rate of T_c suppression with disorder, dT_c/dx, follows the relation $|dT_c/dx|_{\mathrm{Zn}} > |dT_c/dx|_{\mathrm{Fe}} > |dTc/dx|_{\mathrm{Ni}}$ in the Y 1:2:3 system, while in the Y 1:2:4 system it follows the relation $|dT_c/dx|_{\mathrm{Fe}} > |dT_c/dx|_{\mathrm{Ni}} > |dT_c/dx|_{\mathrm{Zn}}$.

At present there exists no successful theory of distorted cuprate superconductors.[10] In fact, even the theory of clean cuprate superconductors is far from satisfactory.[11] Under such circumstances it is not possible to find a reasonable explanation of the observed T_c suppression in the disordered Y 1:2:4 systems. On the basis of the theories of conventional disordered systems[12,13] we expect two kinds of effects of the impurities in the cuprate systems. The first is the elastic pair breaking as in the Abrikosov-Gorkov theory.[12] For an s-wave superconductor the origin of this effect lies in the magnetic moment of the impurity. In cuprate superconductors we have reasons to believe that the superconductivity in these systems is of s-wave type.[14] The other possible effect of the impurities is the direct reduction of the effective pairing interactions.[13,15] This latter effect is expected to be relatively stronger in the distorted cuprate superconductors because, like the orbitals of the Cu atoms, the orbitals of the impurity atoms are also expected to hybridize with the orbitals of the adjoining oxygen atoms, and hence the bosons of electronic of magnetic origin are liable to be affected more effectively.

In the absence of a reliable theory we caricature the two mentioned effects in an empirical manner in terms of the structural parameters of the impurity atoms and the Y 1:2:3 and Y 1:2:4 systems. The parameters which we consider are (1) the chain number per unit cell, c, $c=1$ for the Y 1:2:3 system while $c=2$ for the Y 1:2:4 system; (2) the hole occupancy of the $3d$ state of the isolated Fe^{2+}, Ni^{2+}, Zn^{2+}, and Ga^{2+} ions, n_A, $n_A=4,2,0,0$ for Fe^{2+}, Ni^{2+}, Zn^{2+}, and Ga^{2} respectively; (3) finally, the hole occupancy of the $d_{x^2-y^2}$, $d_{3z^2-r^2}$ or $4s$ states of the Fe^{2+}, Ni^{2+}, Zn^{2+}, and Ga^{2+} ions in the environment of the crystal. In fact, the crystal symmetry will remove the degeneracy of the various $3d$ states.[16] For Fe^{2+}, Ni^{2+}, Zn^{2+}, and Ga^{2+} the relevant states will be $3d_{3z^2-r^2}(2)$, $3d_{x^2-y^2}(2)$, $3d_{x^2-y^2}(0)$, $4s(0)$, respectively, where in parenthesis we have shown the values of the hole occupancy n_p of these orbitals in the environment of the crystal. We find that the simple expression

$$|dT_c/dx| = B_0(a_1+\sqrt{n_A})^c/(a_2+n_p)^{1/c} \tag{1}$$

caricatures the observed features of T_c depression in both the disordered Y 1:2:3 and Y 1:2:4 systems when $B_0 \approx 3$, $a_1 \approx 2$, and $a_2 \approx \frac{1}{2}$.

Let us see what physical information Eq. (1) conveys regarding the suppression of T_c in the considered systems. The fact that Eq. (1) describes T_c depression in the considered systems for $a_1 > a_2$ implies that with increasing chain number the impurities tend to possess effectively more isolated-atomic-like character[17] which is represented here by the hole occupancy n_A. This allows us to give a hint why Fe, which possesses the largest magnetic moment in the isolated-atomic form out of the considered type of the impurities, leads to the largest $|dT_c/dx|$. As far as the believed enhancement of the moment in the Y 1:2:4 systems is concerned, we may verify it by magnetic susceptibility measurements. Other information contained in Eq. (1) is that $|dT_c/dx|$ in Y 1:2:4 increases relatively for all the impurities than in the Y 1:2:3 system. This is because $(a_1+\sqrt{n_A}) > (a_2+n_p)$ and because $C > 1/C$ for the Y 1:2:4 systems as opposed to $C=1/C$ for the Y 1:2:3 system. This latter feature cannot be understood on the basis of enhanced atomic character in the Y 1:2:4 system. This is because in the isolated-atomic form the magnetic moment of Zn is zero so that $|dT_c/dx|$ should have been less in the Zn-doped Y 1:2:4 system than in the corresponding Y 1:2:3 system. Thus, along with enhanced isolated atomic character we expect a significant possibility of direct suppression of the pairing interaction in the Y 1:2:4 system.

In conclusion, we have observed T_c suppression in the described Y 1:2:4 system. The observations are supposed to support a mechanism of T_c suppression in which the moments of the impurities acquire effectively more isolated-atomic-like character in the Y 1:2:4 systems and, at the same time, the direct suppression of the pairing interaction is more significant in the considered system.

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