Dopant interactions in superconducting $YBa_2Cu_3O_7$

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The suppression of T_c by pairs of dopants which substitute for Cu in superconducting $YBa_2[Cu_{0.95}(M_xN_{1-x})_{0.05}]_3O_{7-\delta}$ (M_xN_{1-x} = Ni_xZn_{1-x}, Ga_xZn_{1-x}, Ga_xNi_{1-x}, Fe_xZn_{1-x}) is found to be nonlinear in the concentration x when the dopants occupy both of the inequivalent Cu sites, indicating a strong interlayer coupling. The response is distinctly different for magnetic and nonmagnetic ions. The large suppression due to Zn ions is shown to be correlated with a similar increase in hole density, which is relevant for comparing current theories of s-wave and d-wave superconductivity.

Impurities provide a microscopic probe of the superconducting state. Anderson's theorem for potential scattering from nonmagnetic impurities in conventional s-wave, weak-coupled superconductors predicts no change in the transition temperature T_c, for example.[1] Impurities with magnetic moments, on the other hand, lead to a reduction of T_c.[2] Recent evidence for d-wave superconductivity[3,4] has led to the use of dopants to help distinguish between isotropic s-wave and d-wave superconductivity, since theories predict that even nonmagnetic impurities can suppress T_c in d-wave superconductors.[5] The large decrease of T_c in $YBa_2Cu_3O_{7-\delta}$ per nonmagnetic Zn dopant,[6] apparently contrary to Anderson's theorem, has been taken as evidence against isotropic s-wave superconductivity. Proponents of the spin-fluctuation d-wave theory of high-temperature superconductivity[7–9] have referred to its successful modeling of this Zn behavior as well as the weaker T_c drop from magnetic Ni as a "smoking gun" in support of this viewpoint.[10]

The problem with impurities is that more than one relevant material parameter can be perturbed, making it difficult to unambiguously interpret a drop in T_c. For dopants such as Zn and Ni in $YBa_2Cu_3O_{7-\delta}$, T_c might be affected by the potential scattering from the ions, the magnetic-moment density, or a change in carrier concentration, among other possibilities. Further, the perturbation to the superconducting state may be strongly sensitive to the crystallographic site occupied, e.g., whether the ion resides in the planes or chains of the $YBa_2Cu_3O_{7-\delta}$ structure.

We present here a study of dopant pairs,[11] which substitute for Cu in $YBa_2Cu_3O_{7-\delta}$. In all specimens 5% of the Cu atoms were replaced by Zn, Ni, Ga, and Fe, alone or in pairs. By keeping the total dopant concentration fixed, we hope to have simplified the variation in T_c as the ratio of dopants is varied. In the limit that the potential scattering from these dopants have similar impacts on superconductivity, any change observed in T_c can be attributed to the other parameters: magnetic moment, carrier concentration, and site occupancy. In addition to T_c, we have determined the local magnetic moment per ion, obtained Hall data on the hole densities, and applied various results from the literature to make site assignments, in order to draw some conclusions on the principal factors affecting T_c.

Polycrystalline specimens of $YBa_2[Cu_{0.95}(M_xN_{1-x})_{0.05}]_3O_{7-\delta}$ were prepared with the dopant pairs (Ni,Zn), (Ga,Zn), (Ga,Ni), and (Fe,Zn). Details of the sample preparation have been described elsewhere.[12] Oxygen contents were measured by thermogravimetric analysis,[13] with all δ's less than 0.05 and therefore a minor factor[14] in the subsequent measurements of T_c. The site preferences of these dopants have been investigated by many previous studies, with some variations among the results.[15] The consensus is that the ions with nominal valence 2+ (Ni and Zn) are largely found in the Cu(2) plane sites, while the 3+ ions (Ga and Fe) are predominantly in the Cu(1) chain sites. Anomalous dispersive x-ray work has confirmed this assignment in Ni-doped single crystals,[16,17] where the Cu(2) occupancy was over 95%; preliminary measurements also show a Ga site preference exceeding 80% for the Cu(1) site.[13]

To determine the magnetic nature of each of the dopants, susceptibility measurements were made with a superconducting quantum interference device (SQUID) magnetometer. The results were analyzed as the sum of a Pauli term (χ_0) plus a Curie-Weiss term:

$$\chi = \chi_0 + \frac{1}{3}\frac{\mu_B^2}{k_B}\frac{n_{\mathrm{Cu}}P_{\mathrm{Cu}}^2 + n_M P_M^2}{T-\theta}, \tag{1}$$

where n_{Cu} and n_M are the host Cu and dopant concentrations, P_{Cu} and P_M are the Cu and dopant moments to be determined, and the susceptibilities from all other ions are ignored. The same moment for a given dopant was deduced from both single and codoped specimens, providing a good consistency check. Undoped $YBa_2Cu_3O_7$ showed a Curie-Weiss response with an effective Cu moment of $0.3\mu_B$, whose origin is unclear. The moments for Ni ($2.8\mu_B$) and Fe ($6.2\mu_B$) are in good agreement with Hund's rules estimates assuming Ni^{2+} and Fe^{3+} charge states (3.2 and $5.9\mu_B$, respectively).[18] Zero moments are predicted for Zn and Ga in their expected charge states of Zn^{2+} and Ga^{3+}, but we find an effective moment of $0.2\mu_B$ for both of these dopants, similar to the undoped

material and therefore essentially nonmagnetic.

Simplistic models for the host structure require an average Cu valence of +2.33, corresponding to the two Cu(2) plane sites having Cu^{2+} ions and a Cu^{3+} ion in the Cu(1) chain site.[19] We assume that the density of carriers n can be divided into contributions q_1^{Cu} from the Cu(1) ions and q_2^{Cu} from the Cu(2) sites. A dopant ion M will contribute amounts q_1^M and q_2^M per ion at each site, but if we assume only one site is occupied by a dopant we can write the change in carrier density in $YBa_2[Cu_{1-z}(M_xN_{1-x})_z]_3O_{7-\delta}$ as

$$\Delta n \cong 3z[(1-x)(q_2^N - q_2^{Cu}) + x(q_1^M - q_1^{Cu})]$$
$$= (q_2^N - q_2^{Cu})c_N + (q_1^M - q_1^{Cu})c_M. \quad (2)$$

That is, Δn is simply proportional to the concentrations c_N and c_M of the two dopants. The proportionality constants, e.g., $(q_2^M - q_2^{Cu})$, should be related to the difference in dopant and host valences. Since the proportionality constant for N is explicitly independent of the concentration of M, we refer to this as a noninteracting dopant model.

Hall data provided a measure of how Δn depends on the dopant concentrations. Polycrystalline samples were cut into bars, silver contacts evaporated onto them, and room-temperature measurements of the Hall voltage carried out with a pulsed, 100-mA current in a 3.5-T field. We assume that the carrier concentration n is equal to a proportionality constant α times the Hall number.[20–22] Figure 1 shows the results for the three dopant pairs, which combine nominally 3+ and 2+ ions, i.e., (Ga,Zn), (Ga,Ni), and (Fe,Zn). The straight line fits in accord with Eq. (2) confirm the independent dopant picture with respect to carrier density. The nonzero slopes pass through the hole density value for undoped material, establishing that none of the dopants contribute the same number of holes as the Cu it replaced. We can interpret the Δn as an equivalent difference in the dopant and host Cu chemical valences; these are listed in Table I.

The Hall results for Zn in particular provide an important clue for understanding the anomalously large drop in T_c caused by this nonmagnetic dopant, a well-known effect roughly three times larger than found with Ni, Fe, or Ga dopants. Absent a systematic investigation of the dopant's impact on carrier concentration, this has long suggested an unconventional character for high-temperature superconductivity. Zn is currently the focus of considerable attention with regard to the d-wave spin-fluctuation model.[9,23,24] NMR data[25,26] suggests that Zn supresses spin-fluctuation coupling among Cu ions, and a model, which represents a Zn ion as a small volume devoid of magnetic coupling produced a reasonable fit to the T_c suppression.[9] However, the same theory predicts that T_c should also be sensitive to changes in the hole density. The Hall data in Fig. 1 (and Table I) show an excess hole density for Zn, which is nearly three times greater than for Ni, the *same* factor by which T_c is reduced. The sensitivity of high-temperature superconductors to these dopants clearly is not *prima facie* evidence for unconventional superconductivity; modeling of dopant behavior must include the associated change in carrier density.

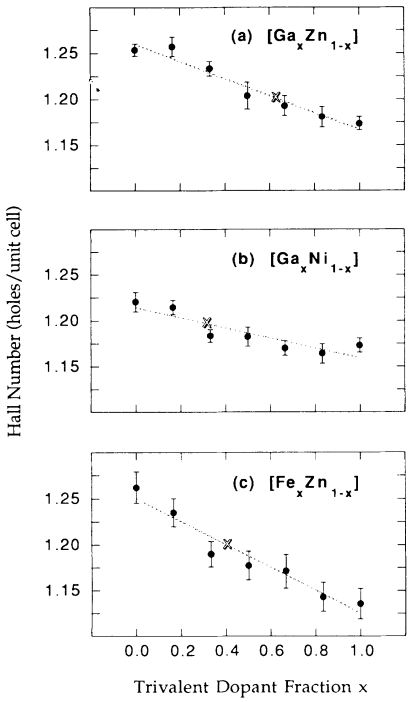

FIG. 1. Hall number vs trivalent dopant fraction x in $YBa_2[Cu_{0.95}(M_xN_{1-x})_{0.05}]_3O_{7-\delta}$, with the dopant pairs (Ga,Zn), (Ga,Ni), and (Fe,Zn), measured at room temperature. All three data sets pass through the value for undoped specimens, marked by a cross.

If the independent dopant behavior seen in the Hall data carries over to the dopants' impact on the superconducting state, then we would expect the drop in T_c to depend linearly on the relative concentration x of the dopants in $YBa_2[Cu_{1-z}(M_xN_{1-x})_z]_3O_{7-\delta}$. Letting $\partial T_c/\partial y_N$ and $\partial T_c/\partial y_M$ represent the rate at which T_c changes upon replacing a fraction y of the Cu by the

TABLE I. For each of the four dopants substituted for Cu into $YBa_2Cu_3O_{7-\delta}$, the first data column gives the dopant magnetic moment determined by a Curie-Weiss fit to magnetic susceptibility. The second column is the effective valence difference for Ni and Zn in the Cu(2) site and for Ga and Fe in the Cu(1) site, determined from the Hall data assuming no antisite occupations (α is the undetermined proportionality between the Hall number and the carrier concentration); the final column lists the resistively determined transition temperature for 5% single-dopant concentration, to be compared with the 91 K value for undoped material.

Dopant	Magnetic Moment (μ_B)	Model Valence Difference	T_c (K), $z = 0.05$
Ni	2.8	$+0.1\alpha$	72
Zn	0.2	$+0.4\alpha$	42
Ga	0.2	-0.2α	76
Fe	6.2	-0.5α	73

dopants N and M, the noninteracting dopant model predicts

$$\Delta T_c = \left(\frac{\partial T_c}{\partial y_N}\right) c_N + \left(\frac{\partial T_c}{\partial y_M}\right) c_M. \quad (3)$$

The superconducting transition temperatures were resistively measured for all of the above codoped Hall specimens, as well as for a number of undoped control samples and single-doped samples with varying dopant concentrations. The change in T_c is approximately linear with (single) dopant concentration through the $z = 0.05$ level for the four dopants (see Table I). Results for codoped specimens are shown in Fig. 2. The nearly linear response of the (Ni,Zn) data shows excellent agreement with the noninteracting, independent dopant model: the drop in T_c is proportional to x, in accord with Eq (3). The (Ni,Zn) data can be explained by a single proportionality factor between Δn and ΔT_c, indicating the critical role played by the carrier concentration in determining T_c.

However, dramatic deviations from noninteracting dopant behavior are seen in the data for (Ga,Zn), where the straight line predicted by Eq. (3) is not observed. The large drop in T_c due to Zn, a nonmagnetic ion in the planes sites, is partially nullified by the introduction of small amounts of Ga, also nonmagnetic but residing in the chains. This compensation is not in proportion to the change in hole density, as indicated by the very nonlinear response. Since neither carrier density nor magnetic moments can account for this, the dual site occupancy must be considered. These data are evidence for strong coupling between the layers of chains and planes.

If Zn is replaced by magnetic Ni, which also resides in the planes, a completely different nonlinear response is seen. A striking suppression of T_c is evident for intermediate concentrations (where the hole densities are about the same as in the undoped material). A nearly identical suppression is seen if the magnetic ion is instead in the chains, as shown in the (Fe,Zn) data of Fig. 2. That is, the nonlinear (Ga,Zn) response transforms to a nonlinear suppression of T_c if *either* Ga *or* Zn are replaced by a magnetic ion. Only when both ions reside in the same sites, i.e., Ni and Zn, do we find agreement with the kind of independent dopant behavior shown previously in the hole density data.

To recapitulate, we have found that the suppression of T_c is directly proportional to the change in carrier density when both dopants occupy only the Cu(2) planes sites. The magnetic character of Ni and conversely the nonmagnetic character of Zn both appear to be inconsequential. When the two dopants separately occupy the planes and the chains, ΔT_c is no longer proportional to Δn. Further, the presence of a magnetic ion appears to drastically alter the nonlinear response, a conclusion that would not be apparent from single-doping studies alone.[27] Overall this is evidence for strong interlayer coupling between the planes and chains in which the dopants perturb T_c in a manner not directly proportional to the total impurity content, the shift in hole density, or simply the magnetic moment density. Our measurements do not identify the mechanism for the interlayer coupling, i.e., the reason why the drop in T_c from a dopant M in the planes should depend on the concentration of dopant N in the chains. Both dopants cause structural perturbations, changes in carrier concentrations, altered charged distributions, and in some cases a localized magnetic moment. The coupling mechanism remains a challenge.

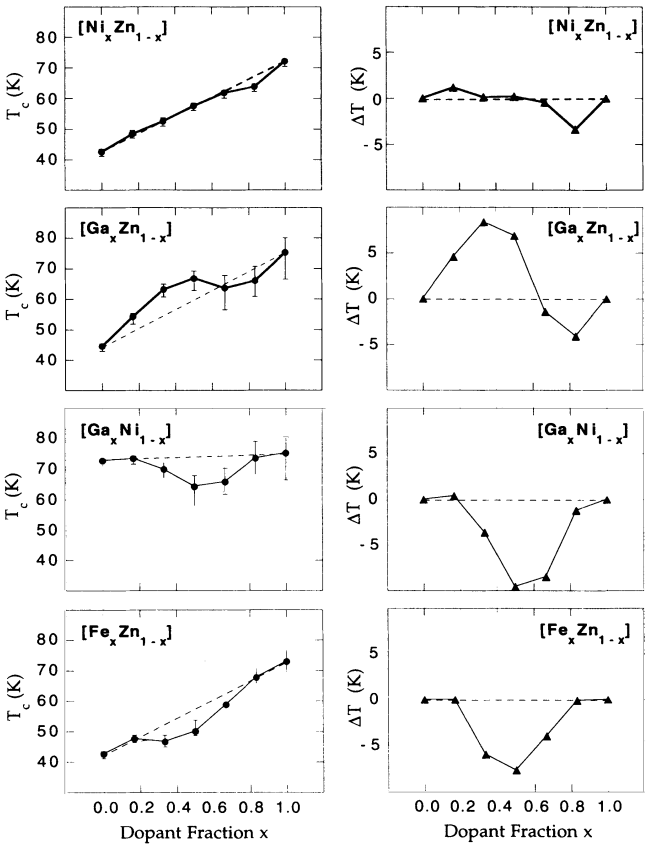

FIG. 2. On the left are the measured T_c's for the four dopant pairs in $YBa_2Cu_3O_{7-\delta}$. Vertical lines denote the 90–10% resistive transition widths; the uncertainties in T_c are smaller. Plotted on the right side is the difference between the measured T_c and the expected value for the independent dopant model, which assumes the change in T_c is just the sum of the T_c changes observed in single-dopant studies.

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