RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 42, NUMBER 13 1 NOVEMBER 1990

Magnetic pair-breaking effects: Moment formation and critical doping level in superconducting $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$ systems (A = Fe, Co, Ni, Zn, Ga, Al)

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(Received 25 June 1990)

We have conducted a systematic study on the effect of Cu-site doping in the $La_{1.85}Sr_{0.15}CuO_4$ system. The relations between T_c and doping level as well as the critical doping levels x_c have been determined accurately for the Fe-, Co-, Ni-, Zn-, Ga-, and Al-doped systems. Every dopant either carries an intrinsic magnetic moment or induces a net moment on the Cu-O_2 plane. The size of the moment is correlated with the suppression of superconductivity, consistent with the magnetic pair-breaking effect. The ground states of the dopants have also been determined.

The ability to dope the Cu site of the high-T_c superconductors with transition or *sp* elements offers an important means to investigate this new class of superconductors.[1,2] The particularly relevant issues in substitution studies are to what degree magnetic and nonmagnetic dopants affect the superconductivity, and how dopants with different electronic structures alter the normal-state transport and magnetic properties. To date, a major body of the Cu-site doping studies[1,2] is related to $YBa_2Cu_3O_7$ (1:2:3) which has two Cu sites. It has been established that 3*d* elements, Fe, Co, Ni, Zn, and *sp* elements, Ga, Al, can all be doped into the Cu sites by various amounts.[1-3] Trivalent ions such as Fe, Co, Ga, and Al prefer the Cu(1) chain site, whereas divalent ions of Ni and Zn go to the Cu(2) plane site. This preference of site locations creates a dilemma, that is, one cannot make a comparative study on the effect of dopants that are not at the same site.

This problem does not exist in the $La_{1.85}Sr_{0.15}CuO_4$ (2:1:4) system where there is only one Cu site. With the motivation of extracting systematic effects of various dopants, we have studied six series of samples $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$ (A = Fe, Co, Ni, Zn, Ga, and Al) made under exactly the same processing conditions. Each sample is fully characterized by x-ray diffraction and confirmed to be single phase. We have accurately determined the relationship between T_c and doping levels, and have studied the magnetic characteristics of these systems. A surprising result is that all the dopants, magnetic or nonmagnetic, induce or carry a substantial magnetic moment due to the unique nature of the Cu-O_2 plane. Furthermore it is observed for the first time that the size of the moment bears a strong correlation with the critical doping level x_c, above which $T_c = 0$. These results suggest a magnetic pair-breaking mechanism, which any viable theory for high-T_c superconductors should account for. We have also found that Fe^{3+} is in the high-spin state, whereas Co^{3+} is in the low-spin state. Ni^{2+}, generally a magnetic ion, is found to carry the lowest magnetic moment among all dopants including the nonmagnetic ones.

In Fig. 1, we present the dopant concentration x dependence of T_c (the bars represent 90%–10% resistivity drop and the dots the midpoint). For every system, T_c varies with x smoothly and monotonically. Above a critical doping level x_c, T_c reduces to zero. The accuracy in x_c, which is determined to be within 0.1%, is assured by using a large number of samples and identical synthesizing conditions. We have also measured the magnetization of various samples under a field of 10 G in both the zero-field-cooled and field-cooled modes. The values of T_c obtained from magnetization measurement are identical to those

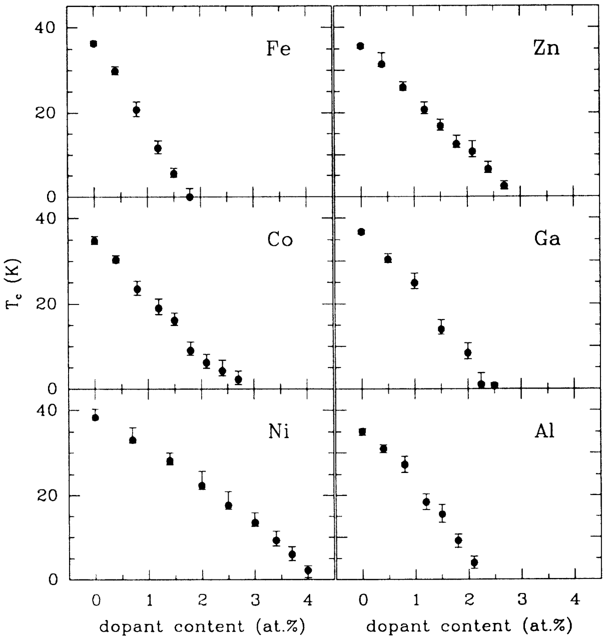

FIG. 1. Variation of T_c with dopant content for $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$ (A = Fe, Co, Ni, Zn, Ga, and Al).

from resistivity measurement. The transition width is also comparable to the resistive transition width. The magnitude of magnetization reduces gradually with increasing doping level, probably due to the increasing pinning strength and penetration depth.

There are a number of interesting features in Fig. 1 when compared with the effect of dopants in $YBa_2Cu_3O_7$. Zn, the most effective in reducing T_c of 1:2:3,[1-4] affects T_c less effectively than Fe in 2:1:4. It is noted that Fe substitutes for the Cu(1) site in 1:2:3. Other nonmagnetic dopants, Al and Ga, become as effective as Zn in destroying superconductivity in 2:1:4, whereas they have little effect on T_c of 1:2:3 because of their Cu(1) site location there. Finally, Ni is the least effective element, as in the case of Ni in 1:2:3. Among all the dopants studied here, Fe suppresses T_c most rapidly, with the smallest x_c of 1.8%, and Ni has the largest x_c of 4.2%. Overall, the effect of dopants in 2:1:4 is much more systematic than in 1:2:3.

One of the immediate questions is whether the effect of dopant is related to its magnetic characteristics. In conventional superconductors, a magnetic impurity is most destructive due to the magnetic pair-breaking effect. In $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$, however, the largest x_c differs from the smallest x_c by only a factor of 2, even though the dopants vary from being strongly magnetic (such as Fe) to nonmagnetic (such as Al, Zn, and Ga). One is tempted to conclude that nonmagnetic impurities are as damaging to high-T_c superconductivity as magnetic impurities. But, as we will show next, this conclusion proves to be superficial.

In order to study the correlation between superconductivity and the magnetic nature of a dopant, we have measured the magnetic susceptibility (χ) using a superconducting quantum interference device (SQUID) magnetometer. Very interestingly, every system, *regardless of a magnetic or nonmagnetic dopant,* exhibits Curie-Weiss behavior, indicating the existence of a localized moment. Figure 2 shows the $\chi(T)$ data for the representative Fe-, Co-, Ni-, and Al-doped 2:1:4 systems. All the curves are shifted arbitrarily for clarity. The solid lines are the fits to the data using the Curie-Weiss relation

$$\chi(T)=\chi_0(T)+\frac{Np_{\text{eff}}^2\mu_B^2}{3k_B(T-\Theta)}\ , \tag{1}$$

where $\chi_0(T)$ represents the background susceptibility which does not change appreciably with doping, N is the dopant content, p_{eff} the effective magnetic moment of a dopant. In our temperature range, to the first-order approximation, we have chosen $\chi_0(T)=\chi_0+\chi_1 T$. The fitting of χ depends sensitively on the magnetic moment, therefore, the values of moment obtained are highly reliable. It is evident in Fig. 2 that all the data can be very well described by relation (1). The sudden drops in χ for some samples at low temperatures are due to the superconducting transitions. The deviations of χ from relation (1) at low temperatures for highly Fe-doped samples are due to the spin-glass orderings. The actual fittings were carried out at temperatures higher than the freezing temperatures. The p_{eff} values obtained from fitting are plotted as functions of dopant concentration for all the systems in Fig. 3 where we assume p_{eff} resides on the dopants. The values of p_{eff} decreases slightly with doping ($0 \leq x \leq 6\%$). Surprisingly, all the nonmagnetic dopants (Zn, Ga, and Al) that cannot carry moments by their atomic structures induce a similar moment, i.e., $1.0-1.2\mu_B$. Fe carries a large moment of $5\mu_B$. Co, often strongly magnetic, carries only a small amount of $1.2\mu_B$, whereas Ni has a moment of only $0.6\mu_B$.

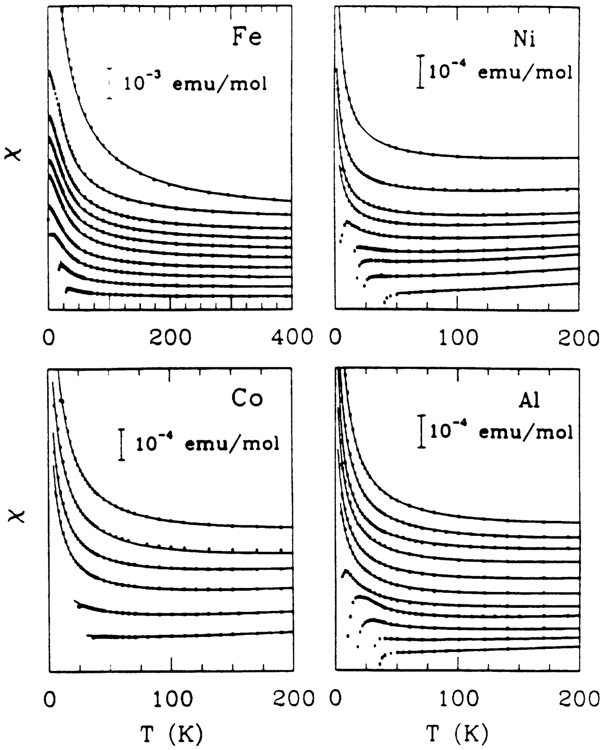

FIG. 2. Magnetic susceptibility χ vs temperature for $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$. Data have been shifted vertically for clarity. The lines are least-squares fits using Curie-Weiss law. (From bottom to top: A = Fe: 0.004, 0.008, 0.012, 0.015, 0.021, 0.024, 0.027, 0.03, 0.04, 0.1; A = Co: 0.004, 0.012, 0.024, 0.03, 0.06, 0.04; A = Ni: 0, 0.02, 0.025, 0.03, 0.034, 0.04, 0.043, 0.048, 0.06; A = Al: 0, 0.004, 0.012, 0.015, 0.018, 0.021, 0.024, 0.027, 0.03, 0.04, 0.06.)

Therefore, in $La_{1.85}Sr_{0.15}CuO_4$, dopants at the Cu site are always *magnetic* in nature. It is meaningless to distinguish magnetic and nonmagnetic dopants based just on their atomic structure. A dopant either retains its atomic moment or induces a net moment in the Cu-O_2 medium. In Fig. 4, we plot the critical doping level x_c versus the magnetic moment of a dopant, illustrating a strong correlation. The Fe-doped system, having a largest localized moment, acquires a lowest x_c. On the other hand, the Ni-doped system with a smallest moment has a highest x_c. Note that the moment of Ni is smaller than others by a factor of 2 or more. In between, the other four systems (with Co, Zn, Ga, Al) have similar moments and x_c values. Such a correlation represents the first observation of an interplay between a dopant moment and the suppression of high-T_c superconductivity. It strongly suggests a magnetic pair-breaking mechanism. In conventional superconductors, x_c corresponds to a critical

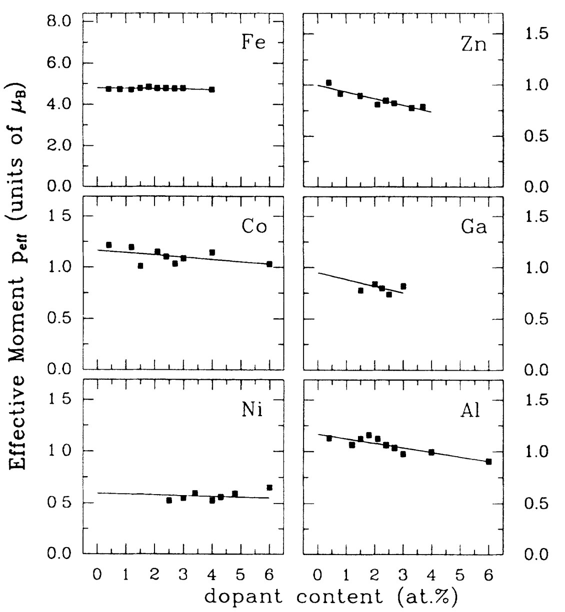

FIG. 3. The dependence of the effective moment $p_{\rm eff}$ on dopant content for $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$. Note the scale difference for the Fe-doped system.

scattering rate between the conduction electrons and impurity spins. Another important result from Fig. 4 is that the degree of the suppression of T_c bears little relation with the valence of a dopant. For example, Zn^{2+} and Ni^{2+} have the same valence, but their corresponding x_c differ a great deal, whereas a similar x_c value is resulted in Zn^{2+} and (Ga^{3+}, Al^{3+}, Co^{3+}) systems with different valence states. We expect that the divalent dopants (Zn^{2+}, Ni^{2+}) would not change the carrier concentration p, and the trivalent dopants (Fe^{3+}, Co^{3+}, Ga^{3+}, Al^{3+}) would reduce p with increasing doping level. However, since x_c is small in every system and is insensitive to the dopant valence state, the suppression of T_c *cannot* be attributed predominantly to any change in p. The oxygen content is believed to be unaffected. In fact, the La_2NiO_4 system[5,6] can be made and 45% of Zn^{2+} can go to the Cu^{2+} site[7] of 2:1:4 without changing the oxygen content.

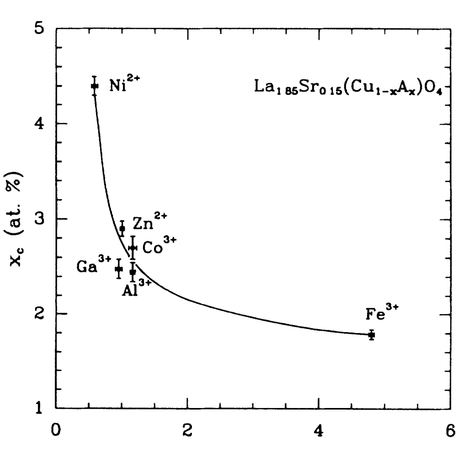

FIG. 4. Correlation between critical dopant level x_c and effective magnetic moment $p_{\rm eff}$. The valence states of various dopants are labeled.

The formation of magnetic moment due to a dopant is an important subject in many respects. It is directly related to the response of the Cu-O_2 plane to a local perturbation, and the response of the electronic state of a dopant to the Cu-O_2 environment. Nonmagnetic dopants such as Zn^{2+}, Ga^{3+}, Al^{3+} have inert full-shell structures ($3d^{10}$ and $2p^6$). Their main role is to locally *remove* the spin of Cu^{2+} ($3d^9$)($S=\frac{1}{2}$). Studying the characteristics of the Cu-O_2 plane with missing spins (i.e., static vacancies) leads to a better understanding of its electronic nature. On the other hand, dopants such as Fe^{3+}, Co^{3+}, and Ni^{2+}($3d^5$,$3d^6$,$3d^8$) can exhibit diverse electronic states depending on their local environment. Therefore, the determination of their states also allows one to probe the Cu-O_2 plane.

As seen in Fig. 3, every nonmagnetic dopant (Zn, Al, or Ga) induces a moment of about $1.2\mu_B$, independent of the electronic structure of a dopant. This is a fundamental fact about the Cu-O_2 plane, revealing its unique electronic nature. It is noted that such nonmagnetic dopants in general do not induce moment in conventional metals. The appearance of the induced moment ($1.2\mu_B$) clearly indicates the highly localized nature of the d state in the superconducting $La_{1.85}Sr_{0.15}CuO_4$. This moment is nothing but the Cu^{2+} moment,[8] which is concealed from susceptibility measurement due to moment compensation in the dynamic antiferromagnetic state or other more exotic states. A nonmagnetic dopant breaks the compensation and creates a net spin of $S=\frac{1}{2}$, hence generating an effective moment $p_{\rm eff}=g[S(S+1)]^{1/2}(=1.9\mu_B)$. The experimental $p_{\rm eff}$ value is close to $1.2\mu_B$, a 35% reduction from the theoretical value. This is due to the hybridization between the $d_{x^2-y^2}$ and p_σ states, which exists even in La_2CuO_4, i.e., the ordered moment m_z is about 20% to 30% lower than the theoretical value of $0.67\mu_B$ (corrected for zero-point motion).[9]

For impurities with nonfilled d shell, one should not only consider the removed Cu^{2+} spin, but also the intrinsic moment of the dopant itself. The $3d$ orbitals in an octahedron are splitted into the triplet ($t_{2g}=xy$, yz, and xz) and doublet ($e_g=z^2$ and x^2-y^2) groups, separated by Δ (the crystal field splitting). Depending on Δ and other factors, a $3d$ ion can be in a low-spin or a high-spin state. Next, we will determine the spin states of Fe, Co, and Ni ions in the Cu-O_2 plane. The valence of Fe in 2:1:4 is 3+ determined from the ^{57}Fe Mössbauer spectroscopy.[10] Fe^{3+}($3d^5$) ion has a high-spin state of $S=\frac{5}{2}$ and a low-spin state of $S=\frac{1}{2}$. Since a Fe^{3+} removes a Cu^{2+} with an effective spin of $S=0.24$ (calculated from $p_{\rm eff}=1.2\mu_B$), the net spin for Fe^{3+} would be $S=\frac{5}{2}-0.24=2.26$ for the high-spin state and $S=\frac{1}{2}-0.24=0.26$ for the low-spin state with an effective moment of 5.43 and $1.14\mu_B$, respectively. Our experimental value is $p_{\rm eff}(\rm Fe)=4.9\mu_B$, indicating unambiguously that Fe^{3+} is in the high-spin state in 2:1:4.

Co can have a valence of $3+(3d^6)$ or $2+(3d^7)$. In $La_{1.85}Sr_{0.15}CuO_4$, it has a moment of $p_{\rm eff}=1.2\mu_B$, therefore the spin of the Co ions has to be $S=0$ (i.e., nonmagnetic). The moment obtained is actually from the Cu^{2+}

To satisfy $S=0$, the only possible state is the low-spin state of Co^{3+}. That is why the effect of the nonmagnetic Co^{3+} on T_c is similar to that of Zn^{2+}, Ga^{3+}, Al^{3+}, with an x_c of 2.5%.

The different spin states of Fe^{3+} and Co^{3+} in 2:1:4 can be understood from the chemistry of these two ions.[11] In a regular octaheral crystal field, a high- (low-) spin state is the result if Δ is less (greater) than the pairing energy P of two electrons in the same orbital. Experimental facts and theoretical calculations show that in an octahedron the d^5 ions (such as Fe^{3+}) are exceptionally stable in their high-spin state, whereas the d^6 ions (such as Co^{3+}) are exceptionally stable in their low-spin state.[11] This has to do with the facts that P is smaller in d^6 than in d^5 and the covalency (hence Δ) of d^6 tends to be stronger than that of d^5.

The size of the Ni moment ($0.6\mu_B$) is more intriguing. The most stable valence state of Ni in the 2:1:4 structure is $2+(3d^8)$. In the high-spin state, $S=1$, the upper d levels, d_{z^2} and $d_{x^2-y^2}$, have one electron each. The low-spin state $S=0$ has a filled d_{z^2} level. If Ni^{2+} was in the $S=0$ state, a moment of $1.2\mu_B$ would be expected as seen in the Zn, Ga, Al, and Co cases. Therefore such a state is unlikely. The high-spin state, however, is most probable. To generate a moment of $0.6\mu_B$, the spin of the Ni^{2+} high-spin state should be no more than 0.32 (after correcting for the Cu^{2+} moment). This low value indicates that both the $d_{x^2-y^2}$ and d_{z^2} levels in Ni^{2+} are strongly hybridized with the neighboring p states.

Therefore, we have resolved the problem of magnetic-moment formation of various dopants in the Cu-O_2 plane. The spin states of Fe^{3+} and Co^{3+} are consistent with their usual chemistry, and their t_{2g} triplets are highly localized. On the other hand, the e_g doublet states of Ni^{2+} are delocalized substantially, resulting in a much reduced moment. Without exception, every dopant (Zn, Ga, Al, and Co) with $S=0$, hence nonmagnetic intrinsically, induces a moment of about $1.2\mu_B$, which is the Cu^{2+} moment. It is shown that, to account for the moment formation of various dopants, the removed Cu^{2+} spin due to doping must be considered. The correlation between x_c and magnetic moment is consistent with the magnetic pair-breaking effect. In the 2:1:4 superconducting state, the largely localized Cu^{2+} spins do not have any long-range ordering, nor do they appear in a Curie-Weiss fashion. However, this unusual magnetic state is believed to play an important role for the high-T_c. Doping creates disorder in this exotic magnetic state, and the magnitude of the disorder can be characterized by the size of the magnetic moment created by a dopant. Our results demonstrate that such a magnetic disorder is extremely detrimental to high-T_c superconductivity, which must be served as a constraint for the high-T_c theory.

This work is supported by NSF Grant No. DMR88-22559.

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