PHYSICAL REVIEW B VOLUME 42, NUMBER 1 1 JULY 1990

Static vacancies in antiferromagnetic La_2CuO_4 and superconducting $La_{2-x}Sr_xCuO_4$

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(Received 1 February 1990)

The effect of static vacancies that eliminate local Cu^{2+} spins has been studied in both the antiferromagnetic and superconducting state of $La_{2-x}Sr_xCuO_4$. Static vacancies induce uncompensated magnetic moments and suppress the three-dimensional Néel state much less effectively than mobile vacancies. Analysis of magnetic susceptibility provides accurately the Cu^{2+} magnetic moment ($\sim 1\mu_B$), which is insensitive to Sr doping, indicating that the d state of Cu^{2+} remains highly localized upon the introduction of mobile vacancy.

One of the essential features shared by all of the high-T_c cuprates is the dramatic collapse of the long-range three-dimensional (3D) antiferromagnetic (AF) order and the appearance of the superconducting state upon the introduction of mobile vacancy. The CuO_2 planes in the parent compounds can be well described in terms of a 2D $S=\frac{1}{2}$ Heisenberg antiferromagnet.[1-4] However, the superconducting state remains elusive. Neutron scattering measurements indicate that the 2D AF fluctuation persists in the superconducting state,[4,5] but with much altered magnetic dynamics from the 2D AF state in the parent compounds.[2] A question of fundamental importance is how doping affects the electronic states of the Cu.[2+] Does the electron in the Cu^{2+} $3d_{x^2+y^2}$ antibonding state remain localized in the highly doped samples, therefore exhibiting substantial localized magnetic moments on the Cu site, or does the $3d$ electron become delocalized resulting in a much reduced or vanished moment in the superconducting state? The confirmation of one of these scenarios will be extremely helpful. The particularly relevant issues are the connection between magnetism and superconductivity, the validity of various models based on localized moment, itinerant magnetism, and nonmagnetic origins. Many techniques, such as muon spin rotation,[6] susceptibility,[7] and neutron scattering[4,8] have been used to study the magnetic characteristics in the superconducting state of $La_{2-x}Sr_xCuO_4$. It is generally agreed that the spins on the Cu^{2+} sites tend to be localized. However, the value of the magnetic moment as inferred from these measurements differs considerably, ranging from a very small value[6,7] to nearly unchanged[5,8] as compared with the Cu^{2+} moment in La_2CuO_4.

In this article, we describe the results of probing the magnetic state in $La_{2-x}Sr_xCuO_4$ by means of the introduction of static vacancy, which is achieved by locally removing spins on the Cu^{2+} square lattice. Experimentally, a small amount of Cu^{2+} ($3d^9$) ions are replaced by Zn^{2+} ($3d^{10}$) ions, which create static vacancies with no spins. The density of static vacancies is controlled by the Zn doping level, while the density of mobile vacancies is dictated by the Sr content, since Cu^{2+} and Zn^{2+} share the same charge state. There are several consequences of static vacancies that deserve investigation. First, a static vacancy will affect the AF ordering in a manner different from a mobile vacancy. Bulut *et al.*[9] have studied theoretically the static vacancies on a 2D Heisenberg $S=\frac{1}{2}$ AF lattice. One of the surprising results is that quantum fluctuations are reduced on the nearest neighbors of an isolated vacancy, whereas on the average they are enhanced. Second, a static vacancy will create a net spin $S=\frac{1}{2}$ (see the following discussion) on a Cu-O_2 plane which otherwise has a compensated AF spin state. The size and the dynamics of this induced net spin are reflected by the magnetic characteristics of the Cu-O_2 plane and may be influenced by the existence of mobile vacancies. Finally, superconductivity will be affected by a static vacancy. Indeed, T_c of $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ is strongly suppressed by substituting Zn into the Cu sites.[10,11] We have made several series of samples. In $La_2Cu_{1-y}Zn_yO_4$, the effect of static vacancies on the 3D Néel state has been studied. In $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$, we have investigated the dependence of the induced Cu^{2+} moment on both the static and mobile vacancies. The samples were made by use of a solid-state reaction method as described in Ref. 10. Oxygen content should not be affected, because Zn^{2+} is in the same charge state of Cu^{2+} and the doping level is low ($<3.7\%$). Recently, a thorough structural study[12] shows that up to 45 at. % of Zn can replace the Cu sites with the same structural type K_2NiF_4. Neutron-diffraction studies[13] also show that Zn ($\sim 7\%$), substituting for the Cu plane site, does not affect the oxygen content in $YBa_2Cu_3O_7$.

Figure 1 shows the temperature dependence of magnetic susceptibility χ of a few samples with $La_2Cu_{1-y}Zn_yO_4$ ($x=0$, 0.013, 0.020). The data were obtained under an external field of 10 kG. The nondoped sample has a well-defined peak which, however, becomes broadened as the Zn impurity is introduced, presumably due to disorder effects. The Néel temperature T_N as obtained from the position of the maximum of the peak (both sharp and broad) decreases consistently with the Zn content. In the inset of Fig. 1, we present the dependence of T_N on two different kinds of vacancies—the mobile vacancy introduced by Sr in $La_{2-x}Sr_xCuO_4$ and the static vacancy by

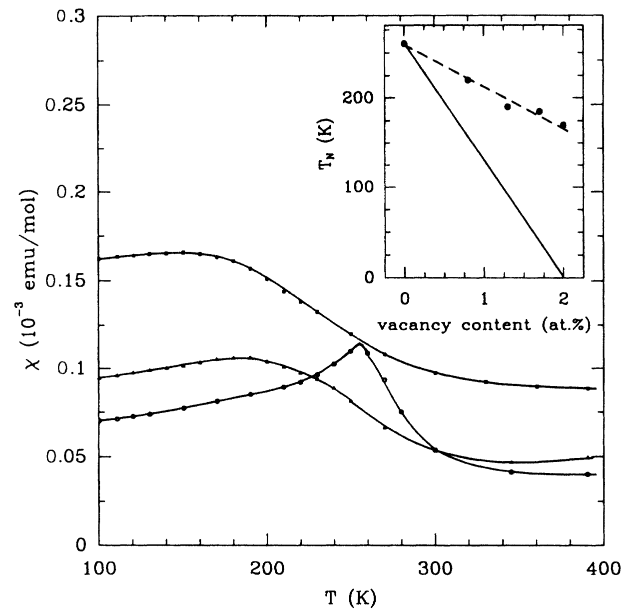

FIG. 1. Magnetic susceptibility χ vs temperature for $La_zCu_{1-y}Zn_yO_4$ ($y=0,0.013$, 0.020). Inset: the dependence of Néel temperature T_N on mobile vacancy content (Sr) (solid line) and on static vacancy content (Zn) (dashed line).

Zn in $La_2Cu_{1-y}Zn_yO_4$. T_N is suppressed to zero with a mobile-vacancy concentration of $x=0.02$, while the critical concentration is $y\sim0.055$ for static vacancies. This difference is largely a consequence of the different locations of the two types of vacancies. In the case of Zn, the spin on the Cu site is eliminated by the Zn impurity, doping with Zn resembles the situation of magnetic dilution. However, the mobile vacancies which reside on the oxygen site provide an extra spin whose coupling with its neighboring Cu spins frustrates the local AF order.[14] Such a frustration effect suppresses the Néel state more effectively than does a static vacancy. A note of caution here is that the static vacancy should not be equated to a simple magnetic dilution, albeit the similarity. The site percolation threshold is 0.41 for a square lattice[15] far exceeding $y_c\sim0.055$. Therefore, the Néel state in La_2CuO_4 appears to be much more susceptible to disorder effect than to percolation.

In both $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ the substitution of the Cu sites by Zn impurity affects T_c detrimentally.[10,11] This was considered a rather surprising result, since Zn^{2+} is a nonmagnetic ion, but our study shows that a Zn impurity is capable of inducing a sizable magnetic moment in the superconducting Cu-O plane. Figure 2(a) shows the magnetic susceptibility χ as a function of temperature for one series $La_{1.85}Sr_{0.15}Cu_{1-y}Zn_yO_4$ ($0\le y\le0.037$). For clarity, the curves are shifted from each other by arbitrary values. The sudden drops in χ at low temperatures for some samples are due to the superconducting transitions. T_c is reduced to zero when the Zn concentration exceeds $y=0.027$. In the normal state of $La_{1.85}Sr_{0.15}CuO_4$, χ decreases as temperature is lowered.[7] With the addition of Zn impurities, there is a gradual increase in χ at low temperatures. Since the characteristics of $\chi(T)$ are reminiscent of a Curie-Weiss behavior, we have used the following relation to analyze our data:

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

Here $\chi_0(T)$ is the non-Curie-Weiss background, N is the number of magnetic ions, p_{eff} is the effective moment in the units of the Bohr magneton μ_B, and Θ is the Curie-Weiss temperature. In the temperature range, to first-order approximation, $\chi_0(T)=\chi_0+\chi_1T$. We found that the fitting of χ depends sensitively on the magnetic moment (i.e., the Curie-Weiss term). The solid lines in Fig. 2(a) are least-squares fits to the data. Relation (1) provides an excellent description of $\chi(T)$ for all of the samples. The values of Θ are in the range -5 to -1 K. The χ data for another series of samples with low Sr content, i.e., $La_{1.95}Sr_{0.05}Cu_{1-y}Zn_yO_4$ ($y=0.01$, 0.013, 0.02, 0.027, and 0.037) are shown in Fig. 2(b). At this Sr concentration, the 3D Néel state has been suppressed and the system is near the insulator-metal transition. Again, we observe a Curie-Weiss behavior in $\chi(T)$ and relation (1) offers excellent fits to the data.

In Fig. 3, we plot the fitted values yp_{eff}^2 ($y=N/N_A$,

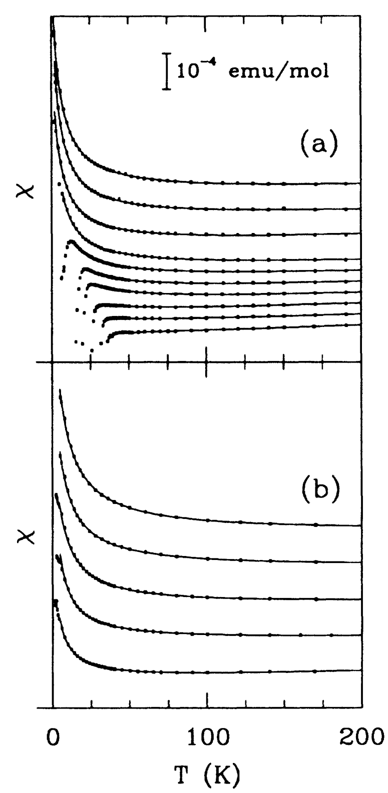

FIG. 2. Magnetic susceptibility χ vs temperature for (a) $La_{1.85}Sr_{0.15}Cu_{1-y}Zn_yO_4$ (from bottom to top: $y=0$, 0.004, 0.008, 0.012, 0.015, 0.021, 0.024, 0.027, 0.033, 0.037); (b) $La_{1.95}Sr_{0.05}Cu_{1-y}Zn_yO_4$ (from bottom to top: $y=0.01$, 0.013, 0.020, 0.027, 0.037). For clarity, all data have been shifted vertically. The line are least-squares fits using Curie-Weiss law.

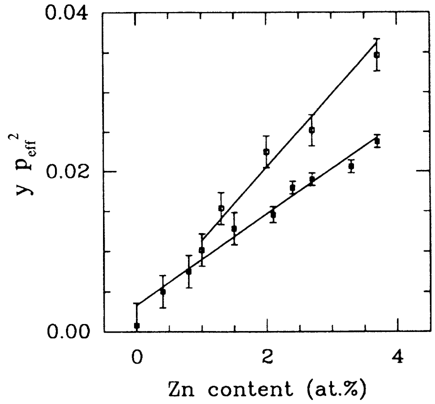

FIG. 3. The fitted values $y\, p_{eff}^2$ in the Curie-Weiss relation vs the Zn content in $La_{1.95}Sr_{0.05}Cu_{1-y}Zn_yO_4$ (square) and in $La_{1.85}Sr_{0.15}Cu_{1-y}Zn_yO_4$ (solid square). The lines are least-squares fits.

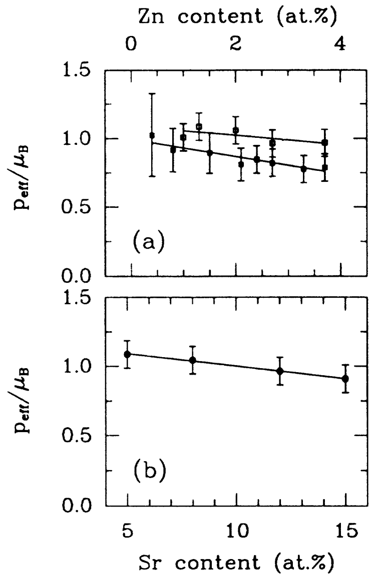

FIG. 4. (a) The dependence of the effective magnetic moment p_{eff} on Zn content for $La_{1.95}Sr_{0.05}Cu_{1-y}Zn_yO_4$ (square) and $La_{1.85}Sr_{0.15}Cu_{1-y}Zn_yO_4$ (solid square); (b) the dependence of the effective magnetic moment p_{eff} on Sr content for $La_{2-x}Sr_xCu_{0.87}Zn_{0.13}O_4$.

where N_A is the Avogadro's constant) versus the Zn concentration for both the $x_{Sr}=0.05$ and the $x_{Sr}=0.15$ series. The value yp_{eff}^2 increases with Zn content y in approximately a linear fashion and yp_{eff}^2 vanishes as y is reduced to zero. Therefore a magnetic moment p_{eff} is induced even though Zn itself does not carry a moment. The different slopes of the lines in Fig. 3 indicate that the magnetic moment per Zn impurity is slightly different in the two series with $x_{Sr}=0.05$ and $x_{Sr}=0.15$. We can also present the data in a more straightforward way. Figure 4(a) shows the induced p_{eff} per Zn impurity as a function of the Zn concentration. The p_{eff} value reduces slightly with increasing Zn concentration and the p_{eff} value is about 20% larger in the $x_{Sr}=0.05$ series than in the $x_{Sr}=0.15$ series. Overall, the p_{eff} values are centered around $1\mu_B$.

To make our study more complete, we have also studied a special series of samples $La_{2-x}Sr_xCu_{0.87}Zn_{0.13}O_4$ $(0.05 \leq x \leq 0.15)$ where we fixed the Zn concentration (static vacancy) and measured the dependence of p_{eff} on the Sr concentration (mobile vacancy). The result is shown in Fig. 4(b). From $x=0.05$ where the sample is an insulator to $x=0.15$ where it is a superconductor the p_{eff} value remains at near $1\mu_B$, reducting slightly from about $1.1\mu_B$ to $0.9\mu_B$.

Neutron-diffraction measurement[4,14] on La_2CuO_4 revealed that the sublattice ordered moment is about $0.5\mu_B$. This value is somewhat lower than the theoretical value $\mu_{Cu}=g\langle S_j^z\rangle=0.67\mu_B$ using $g\cong 2.2$ typical for Cu^{2+}($\langle S_j^z\rangle$ is reduced from $\frac{1}{2}$ to 0.3034 due to zero point motion). But still the $3d$ state of Cu^{2+} is highly localized in La_2CuO_4 and carries a substantial magnetic moment. A fundamental question is whether the $3d$ states remains localized in the metallic or the superconductor state. It will be very helpful if one can monitor the Cu^{2+} magnetic moment as a function of Sr doping. Birgeneau *et al.*[8] have carried out neutron scattering studies on $La_{2-x}Sr_xCuO_4$ $(0.02 \leq x \leq 0.18)$; AF correlations have been observed in the whole doping range. They concluded that the Sr doping does not change the Cu^{2+} moment. But there are large error bars in the integrated quasielastic intensity,[8] which make it difficult to determine the Cu^{2+} moment accurately. Other studies have reached different conclusions. Yamada *et al.*[16] have measured μ_{Cu} in the AF state of La_2CuO_{4-x}; they found that μ_{Cu} decreases from 0.6 to $0.22\mu_B$ as the Néel temperature, which is a measure of the doping level, reduces from 298 to 130 K. In other words, the presence of holes appears to suppress μ_{Cu} substantially. In the analysis of $\chi(T)$ in $La_{2-x}Sr_xCuO_4$, Johnston[7] has also claimed that there is a decrease in μ_{Cu} by as much as a factor of 5 when x reaches about 0.2. Hence, the dependence of μ_{Cu} on hole concentration appears controversial.

The introduction of static vacancy provides us an excellent means to measure the Cu^{2+} moment in $La_{2-x}Sr_xCuO_4$, especially in the metallic and superconducting regions. In an AF state the net spin of the lattice is zero because the spins on the two magnetic sublattices point in opposite directions. A static vacancy which removes a local spin destroys the spin compensation. The net spin induced by a static vacancy is the total lattice spin deviation,[9] i.e., $\langle S_{tot}^z\rangle=\sum_j(\langle S_j^z\rangle-\langle S_j^z\rangle_0)$, where $\langle S_j^z\rangle$ is the expectation value at site j for a system containing a static vacancy, and $\langle S_j^z\rangle_0(=0.3034)$ is the value of a perfect 2D $S=\frac{1}{2}$ Heisenberg antiferromagnet. The sum rule requires $\langle S_{tot}^z\rangle=\frac{1}{2}$ in the ground state of a $S=\frac{1}{2}$ system.[9] Therefore $\langle S_{tot}^z\rangle$ reflects the spin state of a Cu^{2+} site. In $La_{2-x}Sr_xCuO_4$, no 3D Néel state exists for $x \geq 0.02$, but a 2D dynamic AF state persists even in the heavily doped samples $(x=0.18)$.[5,8] Unlike the Néel state, the energy barrier between the spin-up and spin-down state of the induced spin is very small in the dynamic state. Therefore, the induced spin, in effect, behaves like a free spin, whose magnetic susceptibility is of the nature as the Curie-Weiss law. This is precisely what we have observed in Figs. 2(a) and 2(b). By analyzing the $\chi(T)$, one is able to obtain the Cu^{2+} magnetic moment accurately.

From Fig. 4, we can see that Cu^{2+} retains a substantial moment of about $1\mu_B$ both in the lightly doped ($x=0.05$) and heavily doped ($x=0.15$) samples. The Cu^{2+} moment is only slightly affected by the existence of mobile vacancy. The ordered Cu^{2+} moment[4,14] is about $0.5\mu_B$ in La_2CuO_4, which is about 25% lower than the expected value ($0.67\mu_B$). Extrapolating the straight line in Fig. 4(b) to $x=0$, we obtain an effective Cu^{2+} moment of about $1.2\mu_B$. It should be pointed out that this is not the ordered moment, but a moment obtained from the Curie-Weiss relation, i.e., $p_{\text{eff}}=g\sqrt{S(S+1)}$, here $S=\frac{1}{2}$. The expected p_{eff} is about $1.9\mu_B$. Thus the measured p_{eff} value is about 35% lower than the expected value. Such a reduction in p_{eff} most likely is caused by the hybridization between the copper state and oxygen p state. But the fact that the p_{eff} value remains relatively constant over a wide doping range ($0.05\leq x\leq 0.15$) indicates that hybridization effect in the heavily doped superconducting samples is comparable to that in the lightly doped or undoped samples. The d electron states in Cu^{2+} is not strongly disturbed as holes are doped into the Cu-O plane.

Static vacancy is very effective in suppressing high-T_c superconductivity. In $YBa_2Cu_3O_7$, only 10 at. % Zn is needed to bring the sample into the normal state. In $La_{1.85}Sr_{0.15}CuO_4$, the effect of Zn is even more dramatic. We found that the critical concentration x_c above which $T_c=0$ is only 2.8%. Our results reveal that Zn, although nonmagnetic, does induce uncompensated magnetic moments which may act as pair breakers. The highly localized nature of the Cu 3d state indicates that magnetism should be a component in the description of high-T_c mechanism. Our results favor a localized rather than itinerent magnetism approach. Another notable point is that the strong suppression of T_c by Zn is not caused by a large reduction in carrier concentration because of the low Zn doping level (<3 at. %) and its divalent state. Therefore, Zn affect superconductivity in a more fundamental way. In our opinion, strong suppression of T_c without a change in carrier concentration deserves attention, because it allows one to probe the mechanism more directly.

This work was supported by National Science Foundation (NSF) Grant No. DMR88-22559. A work by Chakraborty *et al.* (Ref. 17) on the effect of Zn in La_2CuO_4 has recently been published. The result is similar to that shown in Fig. 1.

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