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Magnetic ordering in $La_2Cu_{1-x}Zn_xO_{4-y}$

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We report the magnetization $M(H,T)$ of $La_2Cu_{1-x}Zn_xO_{4-y}$ for x varying from 0.00 to 0.03. A suppression of the Néel temperature as a function of doping is observed. In contrast, neutron-diffraction experiments show that the low-temperature macroscopic ordered magnetic moment on the copper sites does not change as a function of doping. For applied fields larger than $H_c(T)$, the susceptibility as a function of temperature for the doped samples does not show an obvious signature of ordering at T_N. This is consistent with the material having a macroscopic ferromagnetic moment below T_N for $H > H_c(T)$.

There has been enormous experimental and theoretical interest in the insulating versions of $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{6+y}$ since the discovery of superconductivity in these materials.[1] The insulating versions of these materials are both antiferromagnetic.[2–4] Insulating $La_{2-x}Sr_xCuO_{4-y}$ has been extensively studied and the phase diagram as a function of doping has been found to be extremely rich with phase transitions.[5] In particular, substituting small amounts of Zn for Cu strongly inhibits superconductivity in both $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{6+y}$.[6–8] Zn is a unique dopant, with almost the same ionic radius as Cu (0.75 and 0.73 Å, respectively),[9] and the same ionic valence (+2). However, as Zn has a filled d^{10} shell, it is nonmagnetic. Therefore, it is expected that Zn substitution at the Cu site removes a spin from (creates a spin vacancy) the two-dimensional (2D) antiferromagnetic lattice with little effect on the semiconducting properties of the material. It is of interest therefore to probe the effect of Zn doping on the antiferromagnetic state of insulating La_2CuO_{4-y}, especially with regard to speculations that antiferromagnetic fluctuations which survive into the metallic state could mediate the superconductivity.

We report here the magnetization of $La_2Cu_{1-x}Zn_xO_{4-y}$ for $x=0.00$, 0.01, 0.02, and 0.03, both as a function of temperature and magnetic field. Doping by Zn at the Cu sites decreases T_N. The bulk magnetization as a function of the applied field is superlinear in H above a critical field $H_c(T)$ as reported earlier for $x=0.0$.[10,11] The data is in accord with the presence of an antisymmetric superexchange interaction in the CuO_2 planes which causes the spins to cant out of the plane.[11] Neutron-diffraction results show that the ordered magnetic moment does not change appreciably as a function of Zn doping. The suppression of T_N with increasing x and the insensitivity of the ordered moment to x are consistent with nonmobile Zn introduced spin vacancies in the CuO_2 lattice.

Samples of $La_2Cu_{1-x}Zn_xO_4$ ($x=0.0$, 0.01, 0.02, and 0.03) were prepared from the binary oxides by the standard solid-state reaction technique.[12] The appropriate mixtures were fired to 1100 °C in oxygen for 12 h and then furnace cooled to room temperature. The samples were reground and refired under the same conditions to ensure complete reaction. Powder x-ray-diffraction data were collected on each of the samples both as a check of phase purity and to refine unit-cell parameters. To within experimental resolution ($\approx 0.1\%$), the orthorhombic lattice parameters (a, b, and c) did not change as a function of Zn doping. The magnetic measurements were performed on powdered samples in a Faraday balance described elsewhere.[13] Neutron diffraction was performed on the H4S beam line at the Brookhaven National Laboratory High Flux Beam Reactor. A neutron wavelength of $\lambda = 2.37$ Å was used. Powder-neutron-diffraction studies at room temperature revealed no detectable impurity phase at an intensity level of $\sim 1\%$ of the (200) line in $La_2Cu_{1-x}Zn_xO_{4-y}$ for $x=0.03$.

The temperature dependence of the susceptibility for $H=15$ kG is shown in Fig. 1 for different doping levels. The inset shows T_N^{max} as a function of Zn concentration (shown as ×, the dashed line is a guide to the eye). T_N^{max} was determined from the local maximum in the susceptibility. Shown in the inset (as ○) is T_x, which is another characteristic temperature and will be discussed later. One can clearly see that substitution of Cu by Zn decreases T_N^{max} sublinearly with x. We believe that the maximum in the susceptibility T_N^{max} reflects a lower bound for T_N (the zero-field antiferromagnetic-ordering temperature) as will be discussed later. The increase in χ at low temperatures is probably due to a parasitic phase. By fitting χ below 100 K to a Curie law we obtain 0.04 spin-$\frac{1}{2}$'s per Cu, independent of Zn concentration.

The magnetization as a function of the magnetic field was measured for two compositions ($x=0.01$, 0.03) at temperatures both below and above the Néel temperature. The results are similar to those on the $La_{2-x}Sr_xCuO_{4-y}$ material reported earlier;[10,11] Fig. 2 illustrates this feature. For $T > T_N$, $M(H)$ is essentially linear in H; but for $T < T_N$, $M(H)$ is superlinear in H above some critical field $H_c(T)$. For still higher fields, $M(H)$ becomes linear again. According to Thio *et al.*,[11] the nonlinearity in $M(H)$ for $T < T_N$ is due to an antisymmetric exchange

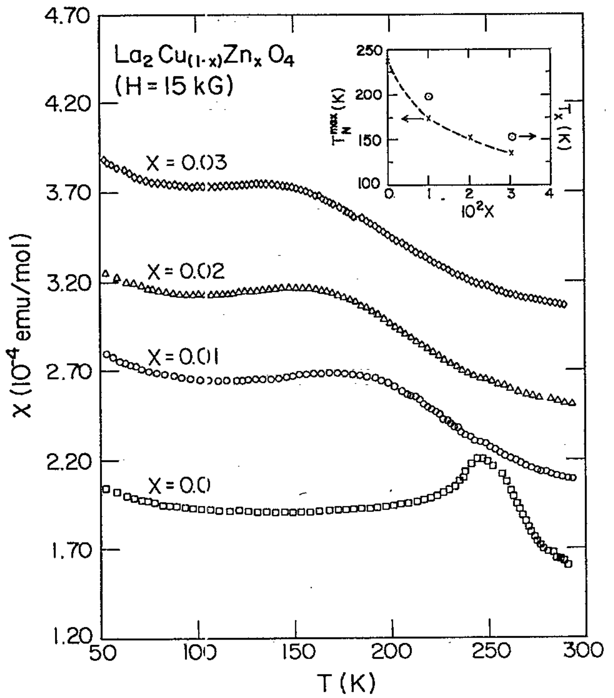

FIG. 1. Magnetic susceptibility vs temperature for $La_2Cu_{1-x}Zn_xO_{4-y}$. Data are corrected for core diamagnetism (Ref. 19). The data for each succeeding curve are displaced by 0.5×10^{-4} emu/mol. The inset shows T_N^{max} (maximum in χ) and T_x (T at which low- and high-field χ diverge).

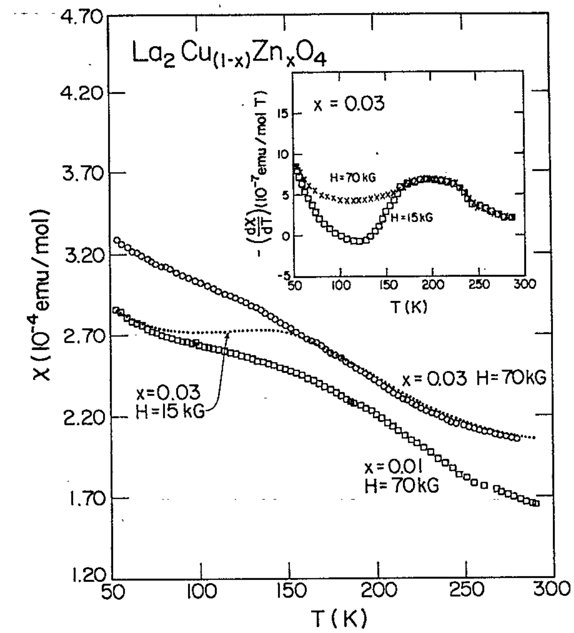

FIG. 3. Susceptibility vs temperature of $La_2Cu_{1-x}Zn_xO_{4-y}$ for $x=0.01$ and 0.03, at $H=70$ kG. Also shown is the low-field χ for $x=0.03$. The $x=0.03$ data is displaced by 0.5×10^{-4} emu/mol. The inset shows $-(d\chi/dT)$ for the $x=0.03$ sample at $H=15$ and 70 kG.

term which causes the spins to cant slightly out of the CuO_2 plane. For $T<T_N$ and $H<H_c$ the canting alternates its direction between planes. At the critical field the canting in all planes abruptly aligns with the component of the field perpendicular to the planes. In our data, this jump in the magnetization is broadened due to the fact that we are using unoriented powder samples.[10]

The susceptibility (defined as $\chi=M/H$) as a function of temperature for $H=70$ kG is shown in Fig. 3 for $x=0.01$ and 0.03. For $x=0.03$ we also show the low-field χ for comparison with high-field χ. The inset shows $-(d\chi/dT)$ for $x=0.03$ at $H=15$ and 70 kG. The high-field χ is significantly larger than the low-field χ for $T<T_N$, and there is no obvious signature of ordering at T_N. This reflects the fact that for $T<T_N$ the system is a macroscopic ferromagnet for $H>H_c(T)$ (Ref. 11) (the canted moments line up in the plane to give a net ferromagnetic moment). For the $x=0.03$ sample, the low- and high-field χ *differ* at roughly $T_x=155$ K [$-(d\chi/dT)$ differs substantially below 155 K as shown in the inset of Fig. 3] which is higher than $T_N^{max}\approx137$ K for this sample. A similar effect was seen in the 1% sample ($T_x=200$ K). Since the superlinearity in $M(H)$ is seen only for $T<T_N$ (Refs. 10 and 11), it is plausible that T_x is a measure of the ordering temperature (upper bound on T_N).

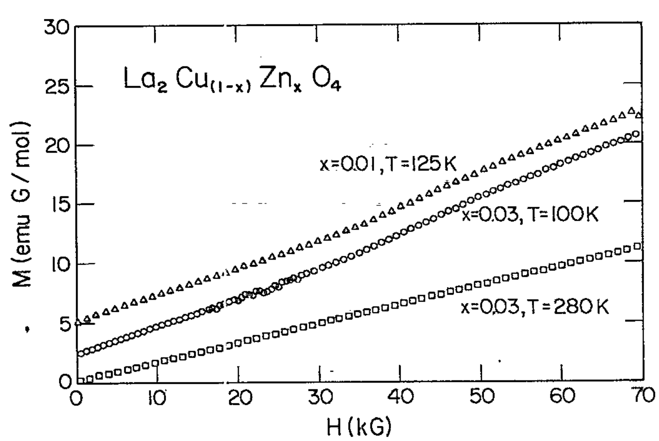

FIG. 2. M vs H at representative temperatures of $La_2Cu_{1-x}Zn_xO_{4-y}$ for $x=0.01$ and 0.03. Each succeeding curve is displaced by 2.5 emu G/mol.

Table I lists the effective moment as a function of Zn concentration as measured by neutron diffraction at 10 K and above the Néel temperature for $x=0.01$, 0.02, and 0.03. The ordered moment does not change as a function of Zn concentration within the error bars ($\pm10\%$). The ordered moment is calculated by comparing the ratio of

TABLE I. Ordered moment and T_{max} tabulated as a function of x for $La_2Cu_{1-x}Zn_xO_{4-y}$.

Zn Fraction	T_N^{max} (K)	T_x	Moment (μ_B)
0	242	···	0.40[a]
1	173	200	0.40 ± 0.05
2	152	···	0.40 ± 0.05
3	135	155	0.40 ± 0.05

[a]See Ref. 3.

intensity of the (100) magnetic peak to the (200) nuclear Bragg peak. Here we assumed the structure to be the same as La_2CuO_4, and used the value reported by Vaknin *et al.*[3] to obtain the ordered moment.

In this study we have identified two characteristic temperatures in the $\chi(T)$ data, T_N^{max} and T_x. The first is the maximum in χ measured at $H=15$ kG, and the second is the temperature *below* which the low-field (15 kG) and high-field (70 kG) χ differ. These values reflect approximate lower and upper bounds on T_N. An alternate effective measure of T_N is the intersection of the tangents to χ (low field) for T below and above T_N^{max}. This would place T_N between T_N^{max} and T_x. This is difficult to resolve given the width of the peaks and hence we only show T_N^{max} and T_x, noting that the true T_N is probably less sublinear with x than T_N^{max}. It may be argued that there may be small changes in the oxygen content as one introduces Zn in the system, which would affect T_N. However, such changes would substantially affect the ordered moment, as measured by neutron diffraction,[5] which is not the case. The question of oxygen stoichiometry has also been addressed by Xiao *et al.*[6] in $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$, where they argue that Zn doping does not change the oxygen content.

Three-dimensional antiferromagnetic order forms once enough energy is gained from the interplanar coupling of short-ranged-ordered regions to overcome thermal fluctuations. Roughly, $k_BT_N \approx J_\perp(\xi_{2D}/a)^2f^2$, where $J_\perp$ is the interplanar coupling, ξ_{2D} is the correlation length for a 2D spin-$\frac{1}{2}$ quantum Heisenberg antiferromagnet, a is the spin-lattice constant, and f is the reduction in the ordered moment at $T=0$. Our results clearly show that T_N is reduced strongly upon Zn doping. This could come about by reduction of $J_\perp$, f, or ξ_{2D}.

Neutron scattering results show that f is unchanged upon doping. We believe that $J_\perp$ is not reduced by Zn doping. Since the planes are shifted relative to each other so that a spin of one plane is centered between four spins of the adjacent planes, interplanar coupling is frustrated. The orthorhombic distortion (the a and c orthorhombic lattice parameters are unequal) of the lattice breaks this frustration, allowing $J_\perp$ to be finite. We found that the lattice parameters do not change as a function of Zn doping, thus we believe that $J_\perp$ does not decrease with doping. Since, roughly $\Delta M(0)H_c(0)=S^2J_\perp$, where $\Delta M(0)$ is the jump in the magnetization at $T=0$, and $H_c(0)$ is the critical field necessary to produce this jump, single-crystal measurements of the above could elucidate the effect of Zn doping on $J_\perp$.

It is likely that Zn doping reduces T_N by removing spins from the 2D lattice, thus reducing ξ_{2D}, but does not drive T_N to zero for low Zn concentrations. In contrast, roughly 2% Sr doping in $La_{2-x}Sr_xCuO_{4-y}$ drives $T_N \rightarrow 0$ (see, for example, Ref. 5). According to Zhang and Rice,[14] the excess hole introduced by Sr doping onto the O orbitals binds into a singlet with one of the Cu spins, effectively removing these spins from the system. However, before the insulator-metal transition (which occurs at $\approx 5\%$ Sr doping) the Sr singlet hole is only weakly localized, perhaps by the relative negative charge of the substitutional Sr impurity,[15] whereas the Zn nonmagnetic site is completely localized. Thus, we believe that the limited itinerancy of the Sr-induced singlet hole extends its effective range, increasing the ability of the Sr dopant to inhibit magnetic ordering, whereas the Zn dopant inhibits magnetic ordering only by local dilution of the spin lattice.

A similar dilution effect is seen in the ordered magnetic moment as measured by neutron diffraction. The presence of 3% Zn dopants does not measurably reduce the low-temperature-ordered magnetic moment. This is consistent with the calculations of Bulut *et al.*,[16] who consider the effects of Zn dopants in a two-dimensional antiferromagnetic bipartide lattice with a quantum spin-wave calculation and exact diagonalization. They find that a single Zn impurity has a small effect on the surrounding order, so that it reduces the ordered moment by less than two spins. If we extrapolate their results to finite Zn concentrations, then we would expect 3% Zn doping to reduce the ordered moment by less than 6%. Such a reduction is outside the resolution of our neutron-diffraction data.

Finally, we would like to comment about the possible effects of Zn impurities at Cu sites in superconducting $La_{1.85}Sr_{0.15}CuO_4$. It has been shown[6] that $\approx 2\%$ Zn doping in this system drives $T_c \rightarrow 0$. We have shown that Zn doping is less detrimental to antiferromagnetic correlations than Sr doping. Since short-ranged antiferromagnetic correlations seem to survive into the superconducting state[17] in which there is 15% Sr doping, then 2% Zn doping should not significantly further reduce these short-ranged correlations. Rather, we propose that they dilute the short-ranged spin order. This is shown in Fig. 4, where we show a region with short-range Néel order and a single-spin vacancy. The vacancy has little effect on the surrounding Néel order (this is consistent with the insulating state calculations of Bulut *et al.*[16]). As a result the region surrounding the vacancy has a net moment which produces a pair breaking field. This could inhibit superconductivity in the same way that a magnetic impurity inhibits T_c in a conventional superconductor, first described by Abrikosov and Gorkov.[18] Xiao *et al.*[6] have already noted that the Abrikosov-Gorkov formula for $T_c(x)$ yields a good fit to their data in $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$.

In conclusion, the Néel temperature decreases as a function of zinc doping. If the maximum in the suscepti-

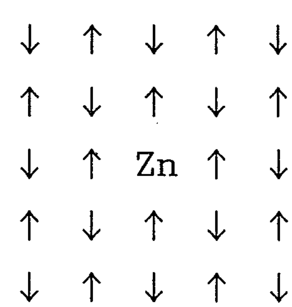

FIG. 4. A region in the CuO_2 plane with short-range Néel order and a single-spin vacancy due to a Zn substitution. The region surrounding the vacancy has a net moment which produces a pair breaking field.

bility is a reasonable measure of T_N then the suppression is sublinear upon doping. It is noted that T_x is less sensitive to increasing Zn concentration. A more accurate determination of T_N could be achieved by measuring the specific heat of these materials; the cusp in the specific heat would then measure T_N. The effective moment, as measured by neutron diffraction, did not change as function of Zn concentration (within our resolution). Thus, doping with Zn is not as detrimental to the antiferromagnetic state as Sr doping. The three-dimensional-ordered antiferromagnetic state in $La_2Cu_{1-x}Zn_xO_{4-y}$ formed below T_N remains similar to that of undoped La_2CuO_4.

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