Magnetic ordering in La$_2$Cu$_{1-x}$Zn$_x$O$_{4-y}$

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We report the magnetization $M(H,T)$ of La$_2$Cu$_{1-x}$Zn$_x$O$_{4-y}$ 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$_x$CuO$_{4-y}$ and YBa$_2$Cu$_3$O$_{6+y}$ since the discovery of superconductivity in these materials. The insulating versions of these materials are both antiferromagnetic. Insulating La$_{2-x}$Sr$_x$CuO$_{4-y}$ has been extensively studied and the phase diagram as a function of doping has been found to be extremely rich with phase transitions. In particular, substituting small amounts of Zn for Cu strongly inhibits superconductivity in both La$_{2-x}$Sr$_x$CuO$_{4-y}$ and YBa$_2$Cu$_3$O$_{6+y}$. Zn is a unique dopant, with almost the same ionic radius as Cu (0.75 and 0.73 Å, respectively), 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$_2$CuO$_{4-y}$, especially with regard to the possibility of antiferromagnetic fluctuations which survive into the metallic state could mediate the superconductivity.

We report here the magnetization of La$_2$Cu$_{1-x}$Zn$_x$O$_{4-y}$ 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 upper critical field $H_c(T)$ as reported earlier for $x = 0.0$. 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. 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$_2$Cu$_{1-x}$Zn$_x$O$_4$ ($x = 0.0, 0.01, 0.02,$ and 0.03) were prepared from the binary oxides by the standard solid-state reaction technique. 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 $(a, b, c)$ did not change as a function of Zn doping. The magnetic measurements were performed on powdered samples in a Faraday balance described elsewhere. 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$_2$Cu$_{1-x}$Zn$_x$O$_{4-y}$ 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 $T_{\text{N}}^{\text{max}}$ as a function of Zn concentration (shown as $x$, the dashed line is a guide to the eye). $T_{\text{N}}^{\text{max}}$ was determined from the local maximum in the susceptibility. Shown in the inset (as O) is $T_s$, which is another characteristic temperature and will be discussed later. One can clearly see that substitution of Cu by Zn decreases $T_{\text{N}}^{\text{max}}$ sublinearly with $x$. We believe that the maximum in the susceptibility $T_{\text{N}}^{\text{max}}$ reflects a lower bound for $T_N$ (the zero-field antiferromagnetic-ordering temperature) as will be discussed later. The increase in $\chi$ at low temperatures is probably due to a parasitic phase. By fitting $\chi$ 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$_x$CuO$_{4-y}$ material reported earlier; 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., the nonlinearity in $M(H)$ for $T < T_N$ is due to an antisymmetric exchange interaction.
FIG. 1. Magnetic susceptibility vs temperature for La$_2$Cu$_{1-x}$Zn$_x$O$_4$. Data are corrected for core diamagnetism (Ref. 19). The data for each succeeding curve are displaced by 0.5x10$^{-4}$ emu/mol. The inset shows $T_R^{\text{max}}$ (maximum in $\chi$) and $T_x$ (at which low- and high-field $\chi$ diverge).

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 $H = 70$ K is shown in Fig. 3 for $x = 0.01$ and 0.03. For $x = 0.03$ we also show the low-field $\chi$ for comparison with high-field $\chi$. The inset shows $-(d\chi/dT)$ for $x = 0.03$ at $H = 15$ and 70 K. The high-field $\chi$ is significantly larger than the low-field $\chi$ 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 $\chi$ 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 $T_R^{\text{max}} \approx 137$ 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 $T_N$).

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 ($\pm 10\%$). The ordered moment is calculated by comparing the ratio of

![Graph](image_url)

**FIG. 2.** $M$ vs $H$ at representative temperatures of La$_2$Cu$_{1-x}$Zn$_x$O$_4$ for $x = 0.01$ and 0.03. Each succeeding curve is displaced by 2.5 emu G/mol.

![Graph](image_url)

**FIG. 3.** Susceptibility vs temperature of La$_2$Cu$_{1-x}$Zn$_x$O$_4$ for $x = 0.01$ and 0.03, at $H = 70$ K. Also shown is the low-field $\chi$ for $x = 0.03$. The $x = 0.03$ data is displaced by 0.5x10$^{-4}$ emu/mol. The inset shows $-(d\chi/dT)$ for the $x = 0.03$ sample at $H = 15$ and 70 K.

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**TABLE I.** Ordered moment and $T_R^{\text{max}}$ tabulated as a function of concentration of La$_2$Cu$_{1-x}$Zn$_x$O$_4$.

<table>
<thead>
<tr>
<th>Zn Fraction</th>
<th>$T_R^{\text{max}}$ (K)</th>
<th>$T_x$ (K)</th>
<th>Moment ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>242</td>
<td>200</td>
<td>0.40*</td>
</tr>
<tr>
<td>1</td>
<td>173</td>
<td>200</td>
<td>0.40 ± 0.05</td>
</tr>
<tr>
<td>2</td>
<td>152</td>
<td>200</td>
<td>0.40 ± 0.05</td>
</tr>
<tr>
<td>3</td>
<td>135</td>
<td>155</td>
<td>0.40 ± 0.05</td>
</tr>
</tbody>
</table>

*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$_2$CuO$_4$, and used the value reported by Vaknin et al. to obtain the ordered moment.

In this study we have identified two characteristic temperatures in the $\chi(T)$ data, $T^\text{max}_N$ and $T_N$. The first is the maximum in $\chi$ measured at $H=15$ kOe, and the second is the temperature below which the low-field (15 kOe) and high-field (70 kOe) $\chi$ 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 $\chi$ (low field) for $T$ below and above $T^\text{max}_N$. This would place $T_N$ between $T^\text{max}_N$ and $T_N$. This is difficult to resolve given the width of the peaks and hence we only show $T^\text{max}_N$ and $T_N$ noting that the true $T_N$ is probably less sublinear with $x$ than $T^\text{max}_N$. 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, which is not the case. The question of oxygen stoichiometry has also been addressed by Xiao et al. in La$_{1.85}$Sr$_{0.15}$CuO$_4$, 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, $k_B T_N \approx J_z (\xi_{2D} / a)^2 / J_z$, where $J_z$ is the interplanar coupling, $\xi_{2D}$ is the correlation length for a 2D spin-1/2 quantum Heisenberg antiferromagnet, $a$ is the 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 $J_z$, $f$, or $\xi_{2D}$.

Neutron scattering results show that $f$ is unchanged upon doping. We believe that $J_z$ 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 $J_z$ to be finite. We found that the lattice parameters do not change as a function of Zn doping, thus we believe that $J_z$ does not change with doping. Since, roughly $\Delta M(0) H_0(0) = S^2 J_z$, where $\Delta M(0)$ is the jump in the magnetization at $T=0$, and $H_0(0)$ is the critical field necessary to produce this jump, single-crystal measurements of the upper could elucidate the effect of Zn doping on $J_z$.

It is likely that Zn doping reduces $T_N$ by removing spins from the 2D lattice, thus reducing $\xi_{2D}$, but does not drive $T_N$ to zero for low Zn concentrations. In contrast, roughly 2% Sr doping in La$_{2-x}$Sr$_x$CuO$_4$—drives $T_N \to 0$ (see, for example, Ref. 5). According to Zhang and Rice, 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, 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., who consider the effects of Zn dopants in a two-dimensional antiferromagnetic biparticle 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 that $\approx 2%$ Zn doping in this system drives $T_c \to 0$. 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 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.). 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. Xiao et al. have already noted that the Abrikosov-Gorkov formula for $T_c(x)$ yields a good fit to their data in La$_{1.85}$Sr$_{0.15}$CuO$_{1-x}$Zn$_x$O$_4$.

In conclusion, the Néel temperature decreases as a function of Zn doping. If the maximum in the susceptibility...
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$_{2}$Cu$_{1-x}$Zn$_{x}$O$_{4-y}$ formed below $T_N$ remains similar to that of undoped La$_{2}$CuO$_{4}$.

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