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Magnetic dilution study in La_2CuO_4: Comparison with other two-dimensional magnets

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The reduction of the Néel point T_N of La_2CuO_4 by substitution of nonmagnetic Mg or Zn for Cu has been studied, with particular emphasis on keeping the oxygen content unaffected. In the low-concentration range ($\lesssim 10\%$), the rate of T_N suppression is found to be the same as in other two-dimensional (2D) Heisenberg magnets such as K_2CuF_4 ($S=\frac{1}{2}$) and K_2MnF_4 ($S=\frac{5}{2}$). While this suppression rate is larger than for 2D Ising magnets, it is much smaller than the rapid T_N reduction upon introduction of holes in La_2CuO_4 through oxygen excess or heterovalent substitution for La. Thus, no unusual quantum magnetic dilution effects are observed in the $S=\frac{1}{2}$ La_2CuO_4 magnet.

The problem of site-diluted magnets is a simple form of the more general percolation or connectivity problem. In spite of the simplicity of the magnetic dilution problem, only a limited number of experiments have been reported. This can be attributed in part to the difficulty in finding magnetic materials that can be diluted without drastic changes of the magnetic interactions (e.g., due to local symmetry and bond-length variations). Examples of two-dimensional (2D) magnets where these problems could be minimized are K_2CoF_4 and Rb_2CoF_4 in which the reduction of the Néel temperature T_N follows closely the theoretical expectations for $S=\frac{1}{2}$ Ising magnets on a square lattice.[1] Here we report magnetic dilution studies on La_2CuO_4, which is isostructural with the cobalt magnets, but with the cuprates being a Heisenberg system. Particular attention has been given to keep the oxygen concentrations constant because T_N of La_2CuO_4 is known to be very sensitive to this parameter.[2] Our results, together with previous studies on other 2D Heisenberg magnets such as K_2CuF_4 and K_2MnF_4, indicate a "universal" initial reduction of the magnetic ordering temperature that is significantly faster than in 2D Ising magnets.

Extensive investigations of the magnetic behavior of La_2CuO_4 have been performed, especially to explore possible quantum magnetic phenomena, expected to be most pronounced in this $S=\frac{1}{2}$ system.[3] It appears, however, that the magnetic properties in La_2CuO_4 are explainable in terms of a classical spin model, although with slightly renormalized (-20%) parameters.[3-7] However, an anomalous rapid depression of the Néel point upon dilution of the magnetic Cu sites has been reported.[8] The main focus of the present study is to clarify this apparent anomaly.

Even though an ideal 2D $S=\frac{1}{2}$ Heisenberg system does not develop long-range order at finite temperatures, La_2CuO_4 undergoes 3D antiferromagnetic (AF) ordering due to the presence of a slight deviation from the ideal system, possibly due to interlayer coupling. Chakraborty *et al.*[8] reported that nonmagnetic, divalent Zn substitution on Cu sites in La_2CuO_4 induces a rapid decline of T_N. The slope of the initial T_N reduction curve in their report was -20 times larger than the theoretical predication for an Ising square lattice and -9 times larger than that of the 2D Heisenberg magnets such as K_2CuF_4 and K_2MnF_4.[1] The T_N reduction due to Cu dilution is to be contrasted to the effects of charge carriers introduced through either oxygen excess or heterovalent substitution (e.g., Sr, Ba) for La.[2,9] The initial T_N reduction by the introduction of hole carriers was found to be comparable with that by Zn substitution reported by Chakraborty *et al.* Furthermore, for $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$, the threshold in δ and x occurs at $\frac{1}{20}$ of the conventional percolation limit (for the 2D square lattice, the site percolation threshold is predicted to correspond to 41% removal of magnetic sites).[1,10] This fast T_N reduction has been attributed to magnetic frustration arising from the competition between AF order in the CuO_2 planes and ferromagnetic coupling among Cu ions induced via hole carriers.

Among nonmagnetic and divalent atoms, the ionic radii of Mg and Zn ions are very close to that of Cu. According to Shannon's study,[11] the ionic radii of Mg, Cu, and Zn in octahedral coordinations are 0.72, 0.73, and 0.74 Å, respectively. In our investigation of the magnetic dilution by Mg or Zn substitution on Cu sites in La_2CuO_4, we find that Mg atoms are very good substitutional ions for simple magnetic dilution study in La_2CuO_4, i.e., Mg ions have a large solubility limit in the La_2CuO_4 structure and Mg substitution in La_2CuO_4 induces little change of lattice constants and lattice symmetry, especially orthorhombicity. The results of our study also indicate that the rapid T_N reduction by Zn substitution reported by Chakraborty *et al.* is probably due to extra oxygen in their specimens and that T_N variation, by Zn substitution only, is similar to that produced by Mg doping. At the end of our report, we compare the studied magnetic dilution effect on T_N by Mg and Zn with that in more conventional 2D magnets.

Polycrystalline pellets of $La_2Cu_{1-x}Mg(\text{or Zn})_xO_4$ were prepared by conventional solid-state reaction in air. The sintered pellets were annealed at 650 °C for 10 h under a N_2 atmosphere to ensure the least amount of extra oxygen in the compounds, which can affect T_N rather drastically. It is noteworthy that extensive investigations of the oxy-

gen stoichiometry of $La_2CuO_{4+\delta}$ indicate that La_2CuO_4 phase can incorporate extra oxygen (not oxygen vacancies) and that the above inert-gas annealing removes the extra oxygen thoroughly, reflected in a T_N above 300 K.[4,12,13] All sintered pellets of $La_2(Cu_{1-x}Mg_x)O_4$ with $x=0$, 0.01, 0.03, 0.05, 0.1, 0.15, 0.2, and 0.25 or $La_2(Cu_{1-x}Zn_x)O_4$ with $x=0$, 0.01, and 0.03 were prepared and post-synthesis annealed next to each other to ensure the same oxygen content throughout the specimens.

Lattice parameters of $La_2(Cu_{1-x}Mg_x)O_4$ compounds were determined by the least-squares method from film x-ray patterns using Cr$K\alpha$ radiation. The upper panel in Fig. 1 displays the measured values for single-phase materials of $x=0$, 0.05, 0.1, and 0.2. The powder pattern of an $x=0.25$ specimen showed second-phase reflections and the lattice constants for $x=0.25$ were identical with those for $x=0.2$. Thus, the Mg solubility limit in the La_2CuO_4 system appears to be surprisingly large, i.e., between 20 and 25 at.%. Copper ions in the La_2CuO_4 structure are coordinated by oxygen octahedra elongated along the b axis [the elongated octahedra is slightly tilted away from the b axis below a structural transition temperature (see below)].[12,14] It appears that the isotropic nature of the electronic configuration of Mg ions induces more isotropic environment at Cu sites causing the increase of a and c and the decrease of b. (Here we use the orthorhombic notation.) We note that the orthorhombicity, directly related to the difference between a and c, is very insensitive to the Mg substitution on Cu sites up to 20%.

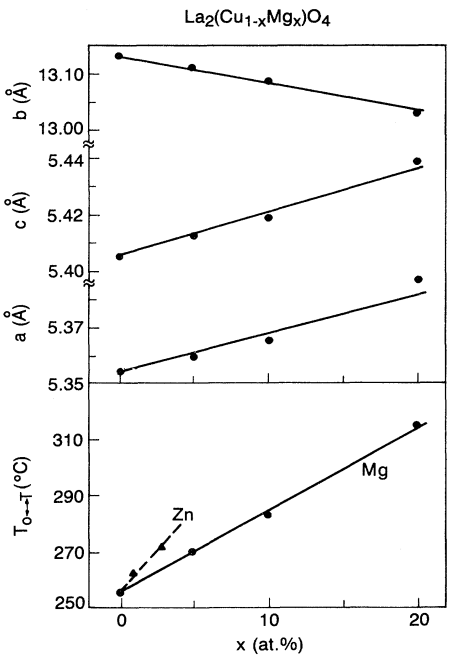

FIG. 1. Evolution of lattice parameters at room temperature as a function of x in $La_2(Cu_{1-x}Mg_x)O_4$ is displayed in the upper panel. The lower panel shows change of the orthorhombic-to-tetragonal transition temperature ($T_{O\leftrightarrow T}$) as a function of x in $La_2(Cu_{1-x}Mg_x)O_4$ (●) and $La_2(Cu_{1-x}Zn_x)O_4$ (▲). Solid lines are drawn as guides for the eyes.

The orthorhombic-to-tetragonal transition for La_2CuO_4 occurs at $T_{O\leftrightarrow T}\approx 530$ K and involves a tilting of the elongated CuO_6 octahedra. The nearest layer magnetic interaction in La_2CuO_4 is frustrated in the tetragonal structure. However, the tilting of CuO_6 octahedra induces nonzero magnetic coupling between nearest layers. Since we may learn how interlayer coupling changes with substitution by investigating the change of $T_{O\leftrightarrow T}$, we measured $T_{O\leftrightarrow T}$ of $La_2(Cu_{1-x}Mg(\text{or }Zn)_x)O_4$. Since the orthorhombic-to-tetragonal transition was found to be an endothermic process, the structural transition temperature was determined by using an Omnitherm Differential Scanning Calorimeter. As shown in the lower panel of Fig. 1, Mg and Zn substitutions induce an increase of $T_{O\leftrightarrow T}$ and Zn substitution has a stronger effect on $T_{O\leftrightarrow T}$ than Mg substitution does. We point out that the Mg substitution causes a rather slow increase of $T_{O\leftrightarrow T}$ ($\sim$10% increase of $T_{O\leftrightarrow T}$ by 20% Mg doping), which, together with the insensitivity of the orthorhombicity to the Mg substitution, suggests qualitatively that there is no dramatic change of interlayer magnetic coupling with the substitution of Mg ions on Cu sites. We also note that according to the report by Chakraborty *et al.*, Zn substitution in low-concentration range induces little change in the lattice constants, similar to the case of Mg doping. However, here we find a faster increase of $T_{O\leftrightarrow T}$ by Zn doping compared to Mg doping, which suggests that Mg atoms are better substitutional ions for simple magnetic dilution studies than Zn atoms.

Magnetic susceptibility χ measurements on Mg or Zn substituted La_2CuO_4 were made in a field of 5 kOe between 2 and 350 K using a Quantum Design SQUID magnetometer. The temperature-dependent susceptibility is plotted in Fig. 2 for representative specimens. Extensive studies showed that the peaklike feature in the χ vs T plot for La_2CuO_4 is associated with AF order of Cu ions and the anomalous shape of the χ peak is due to weak ferromagnetism arising from the tilting of CuO_6 octahedra in the orthorhombic structure. The χ anomaly occurs at $\sim$305 K in the pristine La_2CuO_4 specimen and moves to lower temperatures with increasing Mg substitution. We note that the highest temperature for the χ anomaly ever reported is 326 K for an inert-gas-annealed La_2CuO_4 crystal and the temperature in polycrystalline materials is

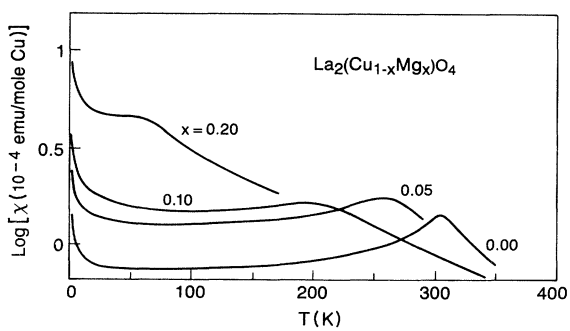

FIG. 2. Logarithm of temperature dependent susceptibility normalized per mole Cu is plotted for various x in $La_2(Cu_{1-x}Mg_x)O_4$.

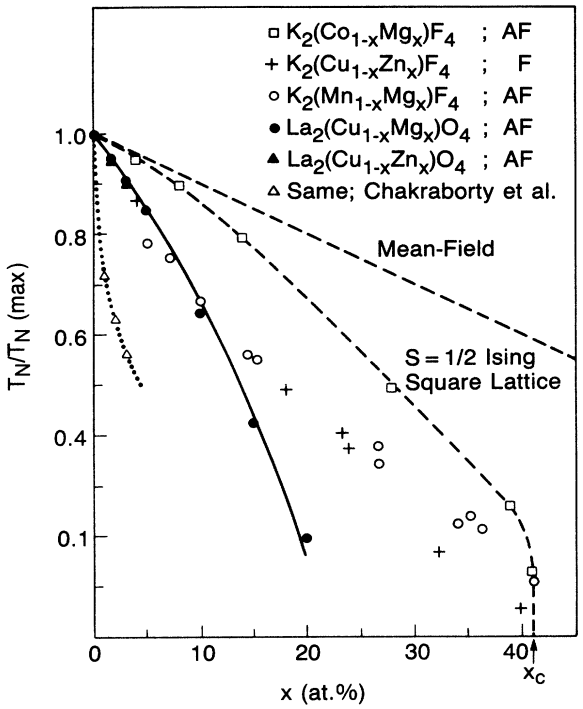

FIG. 3. Normalized Néel temperature [T_N/T_N(max)] vs concentration of nonmagnetic ions at magnetic sites in various quasi-2D magnets. (●, ▲: present work; △: from Ref. 8; the rest: from Ref. 1.) [T_N for ferromagnetic $K_2(Cu_{1-x}Zn_x)F_4$ stands for Curie temperature.]

reported to be lower by ~20 K than 326 K, probably due to poor crystallinity and/or extra oxygen in polycrystalline samples.[2,4] T_N (defined at the temperature where χ reaches its local maximum) as a function of Mg or Zn substitution is displayed in Fig. 3.

Figure 3 also shows various experimental data and theoretical predictions for T_N reduction of diluted 2D magnets. First, all experimental data exhibit, naturally, a faster T_N reduction than the prediction of mean-field theory, which simply states that the long-range-ordering temperature declines linearly with nonmagnetic ion substitution and disappears when magnetic sites are fully occupied by nonmagnetic ions. Second, T_N reduction in a quasi-2D Ising system such as K_2CoF_4 follows rather nicely the prediction for $S=\frac{1}{2}$ Ising square lattice antiferromagnet, of which the critical concentration x_c is identical to the site percolation threshold for a 2D square lattice, i.e., 0.41.[1,10,15] It appears that the critical concentration for Mg-doped La_2CuO_4 is in the range of 20%–25% and Zn substitution in La_2CuO_4, at least in the low doping range, induces a T_N decline slightly faster than, but quite similar to, that by Mg doping. As shown in Fig. 3, the T_N reduction by Zn substitution in La_2CuO_4 reported by Chakraborty *et al.* is much faster than our observation. The facts that their samples were prepared under O_2 atmosphere, contrary to N_2 atmosphere for our final annealing, and that their undoped La_2CuO_4 specimen showed a rather low T_N, i.e., $T_N=242$ K, compared to our $T_N\simeq 305$ K, strongly indicate that their observed rapid T_N reduction by Zn doping is a combined effect of extra oxygen and Zn doping.

Contrary to that in $La_2(Cu_{1-x}Mg_x)O_4$, x_c in $K_2(Cu_{1-x}Zn_x)F_4$ and $K_2(Mn_{1-x}Mg_x)F_4$, 2D Heisenberg magnets, is similar to the site percolation threshold. However, the initial suppression rate of T_N (R_{IS}) tabulated in Table I, in all reported[1,15–17] (to the best of our knowledge) and presently studied 2D Heisenberg magnets including antiferromagnetic $La_2(Cu_{1-x}Mg_x)O_4$ and $K_2(Mn_{1-x}Mg_x)F_4$ are quite similar to each other, i.e., close to $R_{IS}\equiv -\{\partial[T_N(x)/T_N(0)]/\partial x\}_{x=0}=3$. We note that mean-field theory predicts $R_{IS}=1$ and in the case of the 2D Ising square lattice model, R_{IS} is calculated to be -1.3.[17]

It has been estimated that the 3D ordering temperature in quasi-2D Heisenberg antiferromagnets can be written as $k_BT_N \propto J_\perp(\xi_{2D}/a)^2$ where $J_\perp$ is interlayer coupling, ξ_{2D} is 2D magnetic correlation length at T_N and a is the in-plane distance between Cu ions [$(\xi_{2D}/a)^2$ is the number of magnetic ions within the 2D magnetic correlation length].[18] We can generalize the formula for the diluted system as

$$k_BT_N(x) \propto J_\perp\left[\frac{\xi_{2D}(x)}{a}\right]^2(1-x).$$

At least in the case of $La_2(Cu_{1-x}Mg_x)O_4$, the orthorhombicity, determining the interlayer coupling ($J_\perp$), is relatively insensitive to Mg substitution. Thus, if we assume a constant $J_\perp$, $R_{IS}=3$ implies that $\xi_{2D}(x)=\xi_{2D}(0)\times(1-x)$, i.e., ξ_{2D} varies linearly with magnetic dilution

TABLE I. Experimental data on diluted 2D magnets in the K_2NiF_4 structure.

Spin type	Compounds	Substituent	Spin	Coupling	Initial suppression rate R_{IS}[a]	References
Ising	K_2CoF_4	Mg	$\frac{1}{2}$	AF	1.6	15,17
	Rb_2CoF_4	Mg	$\frac{1}{2}$	AF	1.95	16,17
Heisenberg	K_2CuF_4	Zn	$\frac{1}{2}$	F	3	1
	K_2MnF_4	Mg	$\frac{5}{2}$	AF	3~3.5	15,17
	La_2CuO_4	Mg	$\frac{1}{2}$	AF	3	Present work
	La_2CuO_4	Zn	$\frac{1}{2}$	AF	~3.4	Present work

[a] $R_{IS}\equiv -\{\partial[T_N(x)/T_N(0)]/\partial x\}_{x=0}$ where T_N is either the Néel temperature or Curie temperature and x is the concentration of nonmagnetic dopant on magnetic sites.

in the low doping range.

The lack of theoretical understanding of magnetic dilution effect in quasi-2D Heisenberg magnets prohibits any further quantitative analysis. However, our investigation suggests that the magnetic dilution effect on T_N in La_2CuO_4 is similar to that in other quasi-2D Heisenberg magnets such as ferromagnetic $S=\frac{1}{2}$ K_2CuF_4 and antiferromagnetic $S=\frac{5}{2}$ K_2MnF_4. That is, we do not observe any unusual magnetic dilution effect in La_2CuO_4, which, together with various experimental results in Refs. 4–7, suggests that La_2CuO_4 is a rather conventional magnetic system.

In addition to our investigation of the magnetic dilution effects on T_N in La_2CuO_4, we studied the change of superconducting transition temperature T_c in Mg-doped $La_{1.85}Sr_{0.15}CuO_4$ via χ measurements. We found that the T_c reduction by Mg substitution (the data are not shown in this paper) is quite similar to that produced by Zn or Ga doping[19] and superconductivity in $La_{1.85}Sr_{0.15}(Cu_{1-x}Mg_x)O_4$ disappears at $x\simeq 0.025$.

In conclusion, our structural analysis suggests that Mg atoms are particularly good substitutional ions in La_2CuO_4 for the study of simple magnetic dilution effects. Contrary to the earlier report by Chakraborty *et al.*, our results indicate that magnetic dilution effects on T_N in La_2CuO_4, without introducing additional carriers, are very similar to that in conventional 2D Heisenberg magnets such as K_2CuF_4 and K_2MnF_4. Particularly, we find a "universal" behavior of T_N reduction in the quasi-2D Heisenberg magnets at low substitution range ($x\lesssim 10\%$), which is appreciably faster than that in a 2D Ising system. It appears that for small substitution, the dominant effect on T_N stems from a linear decrease in the 2D magnetic correlation length with doping. However, this work finds that x_c is somewhat smaller in doped La_2CuO_4 than predicted by $S=\frac{1}{2}$ Ising models or, for that matter, observed in Heisenberg magnets K_2CuF_4 or K_2MnF_4. It is interesting to observe though that both Mg and Zn depress the superconducting transition temperature T_c of $La_{1.85}Sr_{0.15}CuO_4$ to zero at a value of x about $\frac{1}{10}$ that of x_c for T_N and that $T_c\sim 1/10T_N$, i.e., $dT_c/dx\sim dT_N/dx$ but $d\ln T_c/dx\sim 10d\ln T_N/dx$. We do not believe that this interesting correlation necessarily supports a magnetic mechanism for superconductivity, but rather that this may be a manifestation of a "hidden variable," e.g., structural or electronic, that affects both T_N and T_c.

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