

Evidence for impurity-induced frustration in La_2CuO_4

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Zero-field muon spin rotation and magnetization measurements were performed in $\text{La}_2\text{Cu}_{1-x}M_x\text{O}_4$, for $0 \leq x \leq 0.12$, where Cu^{2+} is replaced either by $M = \text{Zn}^{2+}$ or by $M = \text{Mg}^{2+}$ spinless impurity. It is shown that while the doping dependence of the sublattice magnetization [$M(x)$] is nearly the same for both compounds, the Néel temperature [$T_N(x)$] decreases unambiguously more rapidly in the Zn-doped compound. This difference, not taken into account within a simple dilution model, is associated with the frustration induced by the Zn^{2+} impurity onto the Cu^{2+} antiferromagnetic lattice. In fact, from $T_N(x)$ and $M(x)$ the spin stiffness is derived and found to be reduced by Zn doping more significantly than expected within a dilution model. The effect of the structural modifications induced by doping on the exchange coupling is also discussed.

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La_2CuO_4 has been the subject of intense research activity since the discovery of high-temperature superconductivity (HT_cSC).¹ In fact, besides being the parent compound of HT_cSC , it has been realized early on that La_2CuO_4 is one of the best prototypes of a two-dimensional $S = 1/2$ Heisenberg antiferromagnet on a square lattice (2DQHAFSL).² Accordingly, an impressive amount of theoretical and experimental studies on the effects of charge and spin doping in La_2CuO_4 have followed.^{3,4} In this respect a significant interest has attracted Zn^{2+} $S = 0$ for Cu^{2+} $S = 1/2$ substitution, which is known to be one of the most detrimental elements for HT_cSC .^{4,5} It has been observed that in La_2CuO_4 the substitution of Cu^{2+} with a spinless impurity still can be basically described by the 2DQHAFSL Hamiltonian, with a spin stiffness (ρ_s) renormalized by the spin dilution.⁶⁻¹⁰ Namely, for $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ one has

$$\mathcal{H} = -J \sum_{i,j} P_\infty(x) \mathbf{S}_i \cdot P_\infty(x) \mathbf{S}_j, \quad (1)$$

where J is the superexchange coupling among the nearest-neighbor (n.n.) spins and $P_\infty(x)$ is the probability to find a spin at site i or j for a doping level x , which for $x \leq 0.3$ is well approximated to $(1-x)$.^{9,11} Then, the above Hamiltonian can be mapped onto a 2DQHAFSL Hamiltonian, with $2\pi\rho_s(x) = 1.15J(1-x)^2$.^{2,7} The dilution model is able to describe to a reasonable extent the basic properties of La_2CuO_4 doped with $S = 0$ impurities and, in particular, the main features of the zero-temperature sublattice magnetization $M(x)$ and of the Néel temperature $T_N(x)$.⁷⁻⁹ Nevertheless, recent accurate studies^{12,13} have clearly pointed out that $M(x)$ and $T_N(x)$ experimental data for $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ do not agree with the most accurate description of a 2DQHAFSL achievable through numerical simulations. It is concluded that, although the dilution model is a good starting point to analyze the properties of $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$, a complete understanding of the effect of a spinless impurity in La_2CuO_4 is still missing. Two years ago Liu *et al.*¹⁴ suggested that $S = 0$ impurities might induce magnetic frustration. In fact, if the energy of the lowest unoccupied impurity orbitals is close to the one

of the Cu^{2+} $3d_{x^2-y^2}$ orbital, sizable next-n.n. superexchange couplings may arise and compete with the n.n. coupling.¹⁴ Accordingly, a reduction of $\rho_s(x)$ and of $T_N(x)$ faster than expected according to a dilution model is envisaged.

In order to test if impurity-induced frustration is really relevant, we have performed a systematic comparison of $M(x)$ and $T_N(x)$, determined by muon spin rotation (μSR) and magnetization measurements, in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ and in $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$, for equal doping levels in the range $0 \leq x \leq 0.12$. Since the energy of the unoccupied Mg^{2+} orbitals is far away from the one of the Cu^{2+} $3d_{x^2-y^2}$ orbital, no competing superexchange coupling should be present for Mg doping, while for Zn doping sizable next-n.n. superexchange couplings may arise. It is found that $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$ can be described within a dilution model, provided that minor modifications of J due to the structural deformations are considered. On the other hand, in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ a reduction of $\rho_s(x)$ faster than expected for a dilution model is found. We argue that this decrease of $\rho_s(x)$ indicates that $S = 0$ impurities induce frustration.¹⁴ It is also pointed out that for Zn doping the behavior of $M(x)$ cannot be simply described by a 2DQHAFSL Hamiltonian, since the geometry of the underlying magnetic lattice is progressively changing from the square lattice one to one of a diluted J_1 - J_2 model¹⁵ as the doping increases.

Polycrystalline samples of $\text{La}_2\text{Cu}_{1-x}M_x\text{O}_4$ ($M = \text{Mg}$ or Zn , $x = 0.02, 0.05, 0.075, 0.1, \text{ and } 0.12$) have been obtained by a standard solid-state reaction of 99.99% pure CuO , La_2O_3 , and MgO or ZnO . Stoichiometric quantities of these oxides were thoroughly mixed, pressed into pellets, and multiple sinterings (12–24 h), with intermediate grindings, were performed under air, in the temperature (T) range 900–1100 °C. In order to avoid oxygen excess, a last thermal treatment of 12 h was performed under Ar gas flow at 800 °C. X-ray diffraction showed that the samples were single phase. A Rietveld analysis was then performed using the space group $Bmab$ and the lattice parameters were obtained. The T dependence of the static uniform spin susceptibility, determined with a superconducting quantum interference device magnetometer, is characterized by a peak which marks

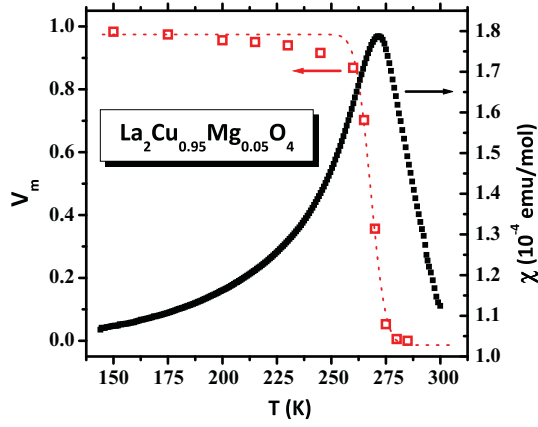


FIG. 1. (Color online) Typical temperature dependence of the macroscopic static uniform spin susceptibility (closed squares, right-hand vertical scale) and of the magnetic volume fraction as derived from μ SR measurements (open squares, left-hand vertical scale) in $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$.

T_N (Fig. 1). The sharpness of the peak confirms the correct oxygen stoichiometry.¹⁶

Zero-field (ZF) μ SR measurements were performed at the ISIS pulsed muon source on MUSR beam line. Below T_N the ZF muon polarization was characterized by clear oscillations associated with the onset of the long-range magnetic order (Fig. 2) and by the corresponding decrease in the longitudinal component of the muon asymmetry.¹⁷ It was noticed that, particularly for

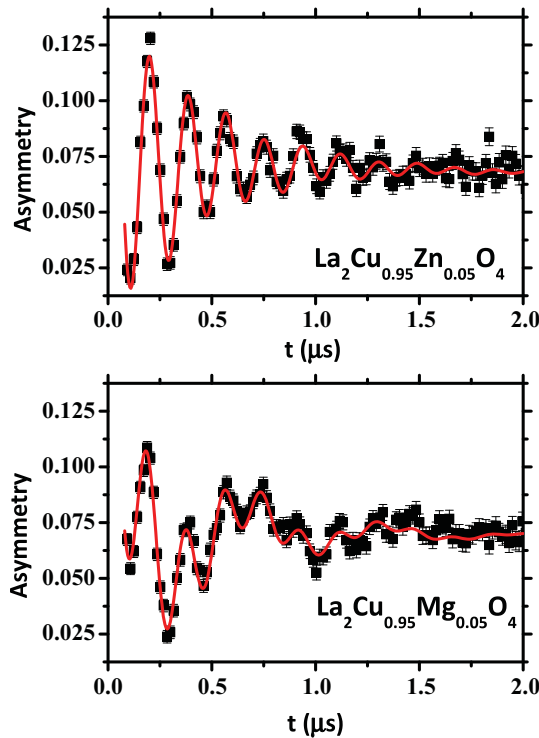


FIG. 2. (Color online) Time evolution of the zero-field muon asymmetry for the $x = 0.05$ Zn-doped (top) and Mg-doped (bottom) samples, at $T = 50$ K. The solid lines are the best fits according to Eq. (2) in the text.

$\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$, two muon precessional frequencies are evident (Fig. 2), indicating two different muon sites. Thus, the decay of the ZF muon asymmetry could be nicely fit to¹⁷

$$A(t) = A_1 e^{-\sigma_1 t} \cos(\gamma_\mu B_1^\mu t + \phi) + A_2 e^{-\sigma_2 t} \cos(\gamma_\mu B_2^\mu t + \phi) + A_3 e^{-\lambda t} + Bck, \quad (2)$$

where γ_μ is the muon gyromagnetic ratio, $B_{1,2}^\mu$ is the local field at the muon sites 1 or 2, which are characterized by different dipolar hyperfine couplings D_i , yielding $B_\mu^i = D_i \langle \mathbf{S} \rangle$, with $\langle \mathbf{S} \rangle$ proportional to the sublattice magnetization. $\sigma_{1,2}$ are the decay rates of the oscillating components, which increase almost linearly with doping¹⁸ owing to the enhancement of the local field distribution with increasing disorder. Bck is a small constant term arising from muons stopping in the sample environment and λ is the decay rate of the muon longitudinal polarization. While in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$, $A_1 \gg A_2$, in the Mg-doped system the amplitude of the two components is similar (Fig. 2). The different ratio A_2/A_1 found for the two systems indicates that, in spite of the same ionic charges and of the nearly equal ionic radii of Zn^{2+} and Mg^{2+} , the lattice potential around the two types of impurity is different. From the drop in the longitudinal component A_3 of the muon asymmetry below T_N it is possible to derive the magnetic volume fraction V_m , since for a powder sample $V_m = (3/2)\{1 - [A_3/(A_1 + A_2 + A_3)]\}$.¹⁷ One observes a sharp increase in V_m at T_N (Fig. 1). In Fig. 3 the T dependence of B_1^μ , normalized to its value extrapolated to $T \rightarrow 0$ $B_1^\mu(0)$, is reported as a function of

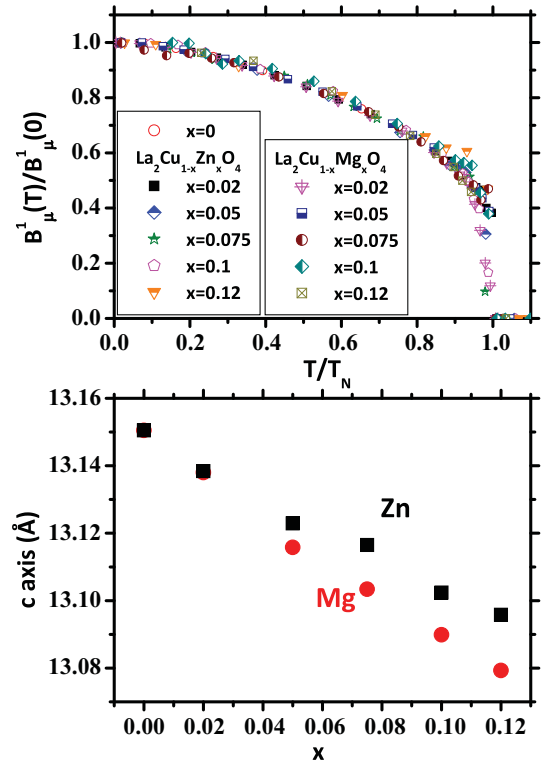


FIG. 3. (Color online) (Top) The local field at muon site 1, rescaled by its value for $T \rightarrow 0$, is reported as a function of $T/T_N(x)$ for $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ and for $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$. (Bottom) Doping dependence of the c -axis length for the same compounds.

T/T_N . One notices that, no matter what is the doping level, the T dependence of the local field at the muon is nearly doping independent once the two aforementioned quantities are properly rescaled. Only for $T \rightarrow T_N$ some scattering in the data is found. However, the analysis of the changes in the critical behavior goes beyond the aim of the present paper.

In Fig. 4 $T_N(x)$ and $M(x)/M(0)$, derived from the ratio $B_\mu^1(x, T \rightarrow 0)/B_\mu^1(0, T \rightarrow 0)$, are reported for the two systems. First of all, one notices that Zn doping induces a more rapid decrease of T_N than Mg substitution. In both cases $T_N(x)$ shows a linear decrease described by $T_N(x)/T_N(0) = (1 - \alpha x)$, with an initial slope $\alpha_{Zn} = 3.52 \pm 0.17$ for Zn doping and $\alpha_{Mg} = 2.7 \pm 0.15$ for Mg doping. Given the energy separation between the first excited Mg^{2+} orbitals and Cu^{2+} $3d$ orbitals, the latter α value should be taken as the one expected for a diluted 2DQHAFSL¹² ($\alpha = 3.196$), reduced by the interplane coupling J_\perp .¹⁹ Remarkably the value derived for α_{Mg} is very close to the one expected if J_\perp is taken to be the one of pure La_2CuO_4 ,¹⁹ suggesting that the interplane coupling is only weakly doping dependent.

In order to properly analyze the results one has first to consider if the lattice deformation induced by doping may cause a significant variation in the n.n. coupling J ,¹⁹ namely, if J in Eq. (1) depends on doping. One can estimate the variation

of $J(x)$ due to the lattice strains in $La_2Cu_{1-x}Mg_xO_4$ on the basis of $T_N(x)$ and $M(x)$ data reported in Fig. 4. In fact, one can write^{2,7,10}

$$T_N(x) = J_\perp P_\infty(x) \left(\frac{M(x)}{M(0)} \right)^2 \xi^2(T_N, x). \quad (3)$$

Since $T_N \ll J$ one has $\xi(T_N, x) \sim \exp[2\pi\rho_s(x)/T_N(x)]$.² Now, assuming that for $La_2Cu_{1-x}Mg_xO_4$ a simple dilution model works, one can write $2\pi\rho_s^{Mg}(x) = 1.15J(x)(1-x)^2$ [see Eq. (1) and Ref. 2]. For a fixed x value one notices from Eq. (3) that an increase in $J(x)$ causes a corresponding enhancement of $T_N(x)$. By taking the experimental values for $T_N(x)$ and $M(x)$, one derives an increase of $J(x)$ by only ~ 40 K for the $x = 0.12$ Mg-doped sample, with respect to $J(0) \simeq 1580$ K.³ This increase is close to the one that could be estimated from the c -axis contraction, by taking into account the c -axis compressibility²⁰ and the variation of J with pressure.²¹ Thus it is concluded that the lattice strains would affect $J(x)$ and α_{Mg} only to a minor extent. Now if one compares the changes in the lattice parameters for both types of substitutions, one finds a similar trend (Fig. 3). Furthermore, one notices that the c axis changes less in the Zn-doped compound, where T_N decreases faster. The above observations show that the major differences in the $T_N(x)$ of the two compounds should not be associated with the effect of the lattice distortions on $J(x)$,¹⁹ but rather with a much faster reduction of the spin stiffness in $La_2Cu_{1-x}Zn_xO_4$, likely due to a frustration of the exchange couplings.

In order to determine the variation of the spin stiffness $\rho_s^{Zn}(x)$ in $La_2Cu_{1-x}Zn_xO_4$, given the similar trend of the lattice parameters in Mg- and Zn-doped samples (Fig. 3), it is reasonable to use the values of $J(x)$ derived for $La_2Cu_{1-x}Mg_xO_4$. From Eq. (3), by taking the ratio of $T_N(x)$ for Zn- and Mg-doped compounds, one can write

$$\rho_s^{Zn}(x) = \frac{T_N^{Zn}(x)}{4\pi} \ln\left(\frac{t(x)}{m^2(x)}\right) + \frac{2.3J(x)t(x)(1-x)^2}{4\pi}, \quad (4)$$

with $t(x) = T_N^{Zn}(x)/T_N^{Mg}(x)$ and $m(x) = M^{Zn}(x)/M^{Mg}(x)$. By taking the experimental data for $T_N(x)$ and $M(x)$, on the basis of Eq. (4), one finds a systematic reduction of $\rho_s^{Zn}(x)$ with respect to $\rho_s^{Mg}(x)$, which reaches $\sim 16\%$ in the $x = 0.12$ sample (see the inset to Fig. 4). Namely, there is a decrease of the spin stiffness for Zn-doped samples, which is much faster than the one expected for a dilution model. Since the reduction of $\rho_s^{Zn}(x)$ cannot be due to lattice strains, as mentioned above, it is clear that the observed variation should be associated with a different effect of Zn and Mg orbitals on the superexchange coupling mechanisms. In particular the marked reduction of the spin stiffness reported in Fig. 4 suggests that Zn doping gives rise to interactions that compete with J , namely, that there is a frustration induced by the impurities, which is consistent with previous theoretical predictions.¹⁴

Now if one considers the behavior of $M(x)$, one finds a similar trend for Mg- and Zn-doped samples (Fig. 4). Again, one can assume that $La_2Cu_{1-x}Mg_xO_4$ behaves as a diluted spin system with $J(x)$ slightly increasing with doping due to structural modifications. Also here it is instructive to observe that the lattice contraction associated with the application of an external pressure yields a small but non-negligible

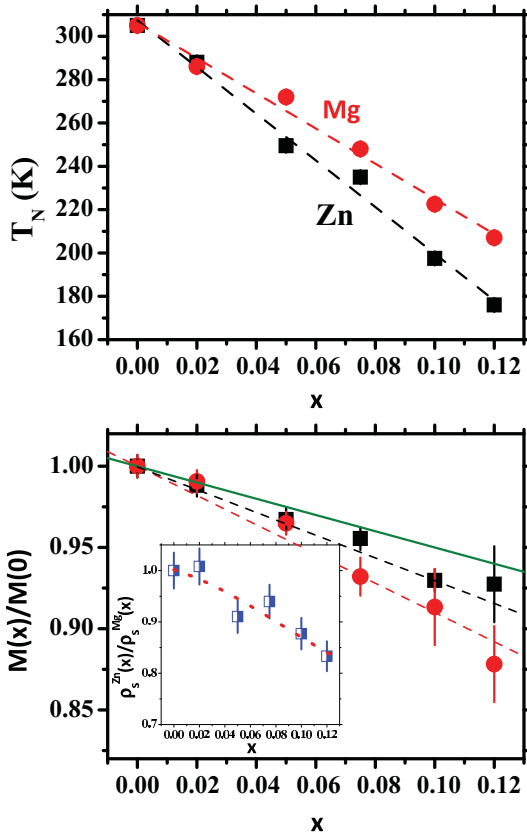


FIG. 4. (Color online) Doping dependence of $T_N(x)$ (top) and of $M(x)/M(0) = B_\mu^1(x, T \rightarrow 0)/B_\mu^1(0, T \rightarrow 0)$ (bottom) in $La_2Cu_{1-x}Mg_xO_4$ and in $La_2Cu_{1-x}Zn_xO_4$ [$B_\mu^1(0, T \rightarrow 0) = 427$ G]. The dashed lines are guides to the eye, while the solid line in the bottom panel shows the behavior expected for a diluted QJ1J2SL (see text). In the inset the ratio of the spin stiffness derived for Zn- and Mg-doped compounds is reported.

reduction of $M(x)$.²² Thus, it is tempting to associate the slight decrease of $M(x)$ found in $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$ with respect to the dilution model¹² to lattice effects. On the other hand, it is not clear why in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$, where $\rho_s^{\text{Zn}}(x)$ is reduced, $M(x)$ does not show a more pronounced decrease. This implies that the more significant reduction of $T_N(x)$ found in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ originates from the decrease of $\rho_s^{\text{Zn}}(x)$ rather than from the one of $M(x)$ [see Eq. (3)].

In order to understand why $M(x)$ reduction is slightly lower in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$, one has to consider that if Zn is giving rise to a next-n.n. coupling, the magnetic lattice around the impurity is no longer a square lattice¹⁴ and the mapping of the microscopic Hamiltonian onto a 2DQHAFSL Hamiltonian should no longer be valid. Indeed, in that case the local configuration around Zn would be more similar to the one found in the diluted $S = 1/2$ J_1 - J_2 model on a square lattice (QJ1J2SL),¹⁵ where the more connected spin texture yields a less pronounced decrease of $M(x)$. In fact, in $\text{Li}_2\text{V}_{1-x}\text{Ti}_x\text{SiO}_4$,¹⁵ a prototype for the diluted QJ1J2SL model, the initial decrease of $M(x)/M(0) \simeq 1 - 0.46x$ is lower than the one found for a diluted 2DQHAFSL (Fig. 4).¹² Still, one has to consider the effect of $\rho_s^{\text{Zn}}(x)$ reduction on $M(x)$. In the framework of the J_1 - J_2 model²³ the observed reduction of $\rho_s^{\text{Zn}}(x)$ would correspond to an effective increase of the ratio J_2/J_1 to $\simeq 0.04$ for $x = 0.12$, which should lead to a corresponding reduction of $M(x)/M(0)$ by only 3.6%,²³ i.e., to

an additional decrease $M(x)/M(0) \simeq 1 - 0.3x$. Thus, taking into account both the effect of dilution and the increase of frustration, the observed decrease of $M(x)/M(0) \simeq 1 - 0.75x$ due to Zn doping (Fig. 4) seems reasonable. Qualitatively speaking, the microscopic configuration that one should find in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ is in between the one of a diluted 2DQHAFSL and the diluted QJ1J2SL model and, accordingly, the $M(x)/M(0)$ curve should stay in between the trend expected for those two models (Fig. 4), as it is observed.

In conclusion, from a comparison of $M(x)$ and $T_N(x)$ in Mg- and Zn-doped La_2CuO_4 , it was found that $\text{La}_2\text{Cu}_{1-x}\text{Mg}_x\text{O}_4$ still can be described in terms of a dilution model with minor corrections due to lattice strains. On the other hand, the marked reduction of the spin stiffness found in $\text{La}_2\text{Cu}_{1-x}\text{Zn}_x\text{O}_4$ indicates that in this latter system competing next-n.n. interactions may arise around the impurity and generate a frustrated magnetic lattice. Also the reduced dependence of $M(x)$ found in the Zn-doped system suggests the presence of a spin texture that is more connected than the one of a diluted 2DQHAFSL, which indicates a different effect of Zn and Mg orbitals in the superexchange coupling mechanisms.

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¹⁸See supplemental material at [<http://link.aps.org/supplemental/10.1103/PhysRevB.83.10.1103/PhysRevB.83.180411>] for the doping dependence of the muon decay rate σ_1 .

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