

Suppression of Antiferromagnetic Order by Light Hole Doping in $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$: A ^{139}La NQR Study

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^{139}La nuclear quadrupole resonance measurements in lightly doped $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ have been performed to reveal the dependence of the magnetic properties of the antiferromagnetic CuO_2 planes on the character of the doped holes and their interactions with the dopant. A detailed study shows that the magnetic properties are remarkably insensitive to the character of the dopant impurity. This indicates that the added holes form previously unrecognized collective structures. [S0031-9007(98)07260-3]

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Full understanding of the character of holes added to cuprate planes and their interactions with the two-dimensional lattice of Cu spins remains a crucial and unsolved problem in the high temperature superconductors. While the detailed mechanism is poorly understood, the rapid suppression of the antiferromagnetic (AF) ordering temperature T_N by doping is clearly related to the disruptive effects of mobile holes: $\leq 3\%$ added holes whether from Sr substitution, addition of interstitial oxygen, or in-plane substitution of Li for Cu [1] suppresses T_N to zero, yet $\sim 30\%$ isovalent substitution of Zn or Mg for Cu is required [2] to produce the same effect. Li- and Sr-doped holes have very different mobilities. For x or $y \approx 0.025$, the room temperature resistivity ρ of $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ exceeds that of $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ by over an order of magnitude [1,3,4]; more strikingly, for Sr doping $d\rho/dT > 0$ for $T \geq 100$ K, in contrast to the negative slope found in Li-doped material for all x and T .

It is well recognized that the 2D cuprates are inclined toward microscopic charge inhomogeneity [5–7]. Evidence for such an effect in lightly doped $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ was obtained from a scaling analysis of the doping y and temperature T dependence of the static susceptibility $\chi(y, T)$ [8] which indicated that the magnetic correlation length is limited to the dimensions of AF domains (finite-size scaling) formed by microsegregation of doped holes into hole-rich domain walls surrounding hole-free, AF domains. Interpretations involving charge stripes have also been proposed [9]. Castro Neto and Hone [10] have examined the influence of doping on the long wavelength properties of a 2D antiferromagnet in a model in which charged stripes cause the exchange coupling J to become anisotropic; this model reproduces the relationship between M_s^0 (M_s is the sublattice magnetization; M_s^0 is that obtained by extrapolation of data for $T > 30$ K to $T = 0$) and T_N as the two are suppressed by Sr doping in $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ [11]. However, using a similar model, van Duin and Zaanen [12] find that T_N is suppressed much more rapidly than M_s^0 with increasing anisotropy (doping).

We have used ^{139}La nuclear quadrupole resonance (NQR) measurements to microscopically examine the

effects of doped holes on the AF spin correlations in $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ ($0.019 < x < 0.025$). We find that the magnetic behavior of lanthanum cuprate is remarkably insensitive to the detailed nature of the dopant, in spite of the differing charge transport associated with the two dopants. In addition to the similarly strong suppression of T_N by doping, we find the identical correspondence between the suppression of M_s^0 and T_N by doping which has been observed in $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$. Further we show, for the first time, that in the vicinity of T_N the dynamical susceptibility, as reflected in the nuclear spin-lattice relaxation rate $2W$, follows a scaling law consistent with the finite-size scaling demonstrated in the static susceptibility by Cho *et al.* [8]. Finally, at low temperature, we find that two peculiar features are very similar in the two systems. These are the very strong peak in $2W$ (at a temperature $T_f = 10\text{--}16$ K depending on x) that indicates freezing of spin degrees of freedom, which is accompanied at slightly higher temperatures (≈ 30 K) by the abrupt recovery of $M_s(T)$, almost to $x = 0$ values.

Thus, while very small concentrations of added holes induce a range of characteristic magnetic properties which are entirely insensitive to the nature of the dopant, the transport properties are very sensitive to the dopant. Unable to understand these contrasting behaviors as arising from properties of individual holes, we conclude holes form collective structures. We will argue that holes form charged, antiphase domain walls [13] which surround mobile domains in which the phase of the AF order is reversed. Such mobile domains will suppress the time-averaged static moment thus suppressing AF order and M_s . These domain structures will have contrasting interactions with in-plane vs out-of-plane dopants (e.g., stronger scattering by in-plane impurities) which explain the different transport behaviors, while the universal magnetic properties can be understood as long as the domains are sufficiently mobile that they move across a given site rapidly compared to a measurement time.

Three powder samples of $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ (labeled A1, B1, and B2) were prepared from starting material containing concentrations x_{nom} of Li as described elsewhere

[1]. Table I shows various measured properties of these samples; definitions of the parameters shown and the means by which they were determined will be discussed in what follows. All the samples were annealed in flowing nitrogen gas after sintering to minimize excess oxygen, whose motion can contribute to ^{139}La spin-lattice relaxation at high T [11,14]. Annealing in nitrogen eliminated this contribution in our samples. The smaller value of x relative to x_{nom} for sample A1 was deduced from its higher value of T_N relative to sample B1. ^{139}La ($I = \frac{7}{2}$) NQR and relaxation rate measurements in $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ were performed for $4 < T < 300$ K on both the $2\nu_Q$ ($\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$) and $3\nu_Q$ ($\pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$) transitions. The spectra were obtained by plotting the integrated intensity of the spin-echo signal as a function of spectrometer frequency. The nuclear spin-lattice relaxation rate was measured by monitoring the recovery of the magnetization after saturation with a single $\frac{\pi}{2}$ pulse.

The ^{139}La NQR results for the three samples are summarized in Fig. 1. Below T_N , the ordered Cu moment generates an internal magnetic field \mathbf{H} at the ^{139}La site which splits the NQR line into a doublet with frequencies ν_1 and ν_2 . The magnitude of the splitting, $\Delta \equiv \nu_1 - \nu_2$, is a direct measure of the component $H_z = H \cos \theta$ of the internal field \mathbf{H} at the La site along the principal (\hat{z}) axis of the electric field gradient (EFG) tensor [9] (θ is the angle between \mathbf{H} and \hat{z}). The two frequencies for the $2\nu_Q$ transition are given by $\nu_{1,2} = 2\nu_Q \pm (\gamma_n/2\pi)H_z$ where the nuclear gyromagnetic ratio $\gamma_n/2\pi = 601.44$ Hz/G. As shown in Fig 1(a), for $T > 30$ K, Δ is suppressed by doping, and then displays an abrupt increase below 30 K. Similar effects have been observed in recent μSR and neutron scattering measurements in $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ [15]. The solid curves in Fig. 1(a) are fits of the temperature dependence $\Delta(T) = \Delta_0(1 - T/T_N)^\beta$ to the data for $T > 30$ K; we find $\beta = 0.44 \pm 0.01$. The magnitudes and temperature dependence of ν_Q for a given doping is almost identical to that found in Ref. [11]; the linewidths are also quite comparable: 110, 120, and 140 kHz at 250 K for our samples A1, B1, and B2, respectively.

Figure 1(b) shows the T dependence of $2W$, which displays a strong peak at $T = T_f = 10\text{--}16$ K and a weak peak in the vicinity of T_N . $2W$ was obtained by fitting the recovery data to the theoretical expression for magnetic

TABLE I. Properties of the three samples: A1, B1, and B2.

	A1	B1	B2
x	0.020	0.020	0.025
x_{nom}	0.019	0.020	0.025
T_N (K)	180 ± 5	145 ± 5	85 ± 10
E_a/k_B (K)	120	123	117
Δ_0 (kHz)	212	193	120
T_f (K)	11	15	16
T_N^* (K)	187	163	114
C	0.042	0.038	0.020
$Cx^2 \times 10^5$	1.52	1.52	1.25

relaxation and for single pulse saturation [16]. For $T > T_f$, this expression fits the data well, indicating a single rate arising from magnetic fluctuations. Although the rate becomes distributed below T_f (consistent with freezing in an inhomogeneous distribution of internal fields), the same fitting procedure was applied to data for the first decade of recovery. While this increases the uncertainty in $2W$, we find that varying the fitting procedure has essentially no effect on the position of the peak at T_f .

As seen in Fig 1(b), $2W(T)$ is the same at the $2\nu_Q$ and $3\nu_Q$ transitions in sample A1, establishing that $2W$ is due to a magnetic rather than structural mechanism. In addition, we note that $2W$ decreases with increasing T for $T > T_N$ in contrast with the results in $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ which show an enhancement of $2W$ at high T due to the motion of excess oxygen [14]. Thus, annealing to remove excess oxygen enables us to obtain, for the first time, intrinsic data for spin dynamics above T_N that are isolated from any significant influence by mobile oxygen.

Our discussion will focus on two aspects of the data: (i) the anomalous behavior of both the static and the dynamical magnetic properties at low T , and (ii) the broad and weak peak in $2W$ around T_N , which contrasts with the sharp peak at T_N observed in, e.g., undoped $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ [17]. These results are, overall, very similar to those found in $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ [9,11].

The strong low- T peak in $2W$ clearly indicates freezing of spin degrees of freedom. Analyzing the data in terms of activated behavior, [$2W(T) \propto \exp(E_a/k_B T)$] as

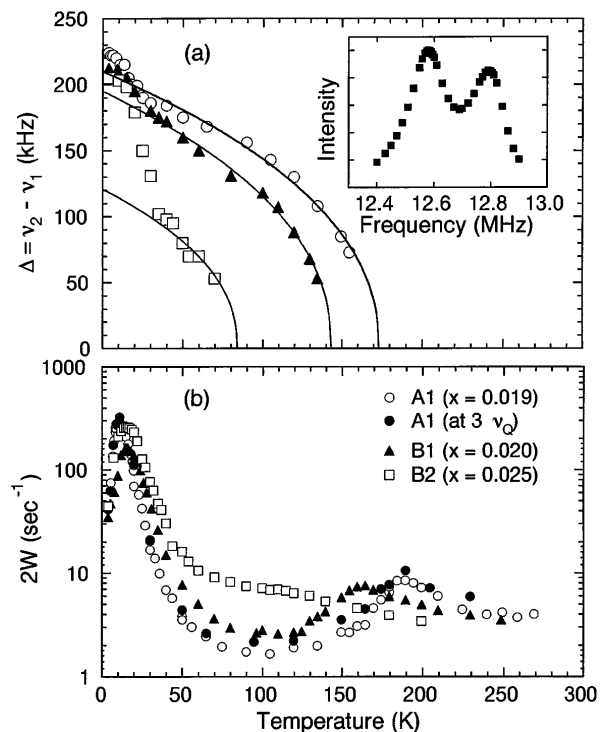


FIG. 1. ^{139}La NQR in $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$: (a) $\Delta \equiv \nu_1 - \nu_2$ vs T . Solid curves are fits to the behavior $\Delta(T) = \Delta_0(1 - T/T_N)^\beta$, $\beta = 0.44 \pm 0.01$. The inset shows the NQR spectrum from sample B2 ($x = 0.025$) at 4 K. (b) $2W$ vs T .

shown in Fig. 2, gives values of E_a (see Table I) similar to those in $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$, where $E_a/k_B T_f = 8.9$, and $T_f \approx 11\text{--}16\text{ K} \Rightarrow E_a/k_B \approx 100\text{--}145\text{ K}$ [11]. Thus, the spin freezing is independent of the dopant, and, consequently, spin freezing is not solely determined by binding of holes to the dopant. We note that $T_f(x)$ (Table I) does not satisfy the empirical relation $T_f = (815\text{ K})x$ obtained in Ref. [11], but the relationship between T_f and T_N is the same in both systems. Such disagreement may arise from a discrepancy in the actual hole-doping level.

We turn now to the behavior of $2W$ in the vicinity of T_N . We find a strong doping dependence of the width of the $2W$ peak as found in the static susceptibility by Cho *et al.* [8], and our results support the finite-size scaling proposed there. To isolate the behavior near T_N from contamination by the tail of the spin-freezing peak at T_f , we first correct the $2W$ data by subtracting the fitting results in Fig. 2 (solid lines). Results are shown in Fig. 3(a). The observed behavior cannot be understood in terms of conventional critical behavior [17]. There, the T -dependent growth of ξ is set by the exchange coupling constant J , and this determines the width of the peak on the high- T side. The strong x dependence of the width then leads to the implausible conclusion that J is strongly x dependent. Nonetheless, it is clear that the behavior of $2W$ around T_N should reflect cooperative behavior of correlated spins near their ordering temperature.

The peak in the static susceptibility observed at T_N is due to the small canting of the ordered moment which arises through the Dzyaloshinski-Moriya interaction. In undoped La_2CuO_4 the shape of this peak is well described by theory [18]; however, with doping the peak broadens and this description is no longer adequate. Cho *et al.* argued that rather than increasing exponentially with decreasing temperature, $\xi(T)$ in lightly doped $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ is limited by confinement to AF domains of size L defined by hole-rich domain walls [8]. They were successful in describing the doping dependent shape of the peak in $\chi(y, T)$ (for $T > T_N$) for a range of y through the scaling relation $\chi(y, T) = \chi\{f(y)[T - T_N(y)]\}$, and they identify $f(y) \approx 0.02/y^2$ with L^2 . If this peak shape is indeed due to $\xi(T)$, consistency of the scaling of $2W/T$ and the static susceptibility is expected since

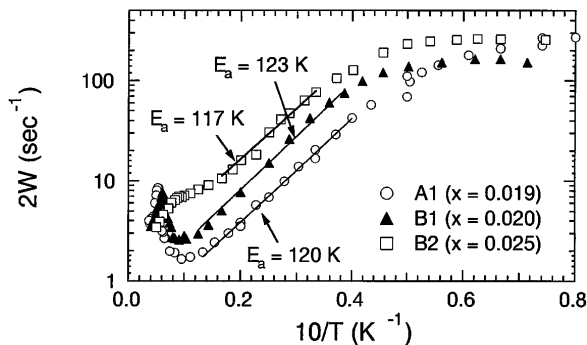


FIG. 2. $2W$ vs $10/T$. Solid lines are fits to the activated behavior $2W \propto \exp(E_a/k_B T)$.

both the static and dynamic susceptibilities (χ' and χ'' , respectively) are determined by the same T -dependent ξ .

We find that the peak in $2W(T)$ occurs at $T = T_N^*$ different from the peak in $\chi(T)$ [marked by arrows in Fig. 3(a); see also Table I]. Given the incomplete understanding of $\chi(T, x)$ for finite x , the peak in $2W$ is likely the better indicator of the temperature at which local AF ordering occurs. Although not understood, we believe this phenomenon is a general feature of lightly doped lanthanum cuprate, and is more prominent in our data because the obscuring effects of mobile excess oxygen at temperatures comparable to T_N have been eliminated here. We find that $2W(T, x)$ exhibits the same scaling behavior with the same scaling function $f(x) = (0.02/x)^2$. The strength of the peak in $2W$ is strongly x dependent, and we apply a normalization factor $C(x)$,

$$\frac{2W}{T}\{x, T\} = C(x) \frac{2W}{T}\{f(x)[T - T_N^*(x)]\}. \quad (1)$$

The data scaled in this way are shown in Fig. 3(b), and we find $C(x) \approx (0.004/x)^2$ as shown in Table I. Given the discrepancy between T_N and T_N^* , these data cannot be taken as demonstrating scaling of $2W$; however, our finding that the same scaling function $f(x)$, when combined with a normalization factor also proportional to $1/x^2$, leads to consistent scaling behavior provides important corroboration for the finite-size scaling hypothesis of Cho *et al.* [8].

The reduction of $2W/T$ associated with limitation of the size of correlated domains is not unexpected. The spin-lattice relaxation rate is given by $2W/T \sim$

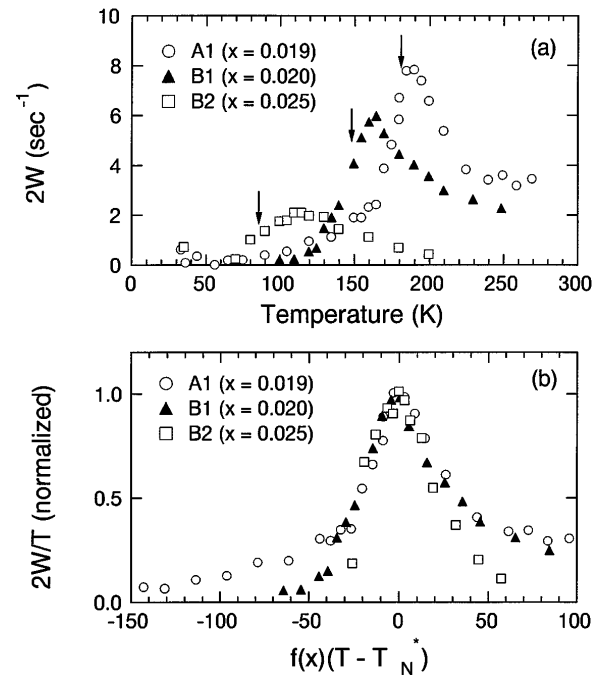


FIG. 3. (a) T dependence of $2W$: $2W$ data are corrected for the contribution from the spin-freezing effects represented by the solid lines in Fig. 2. The arrows indicate T_N . (b) Plots of normalized $2W/T$ as a function of $f(x)(T - T_N^*)$ with $f(x) = (0.02/x)^2$ (see text for details).

$\sum_q A^2(q) [\chi''(q, \omega)/\omega]$, where $A(q)$ is the (sample independent) hyperfine coupling constant. If the spectrum of spin fluctuations is described by a Lorentzian distribution with a characteristic frequency Γ , then $\chi''(q, \omega)/\omega \sim \chi'(q)/\Gamma$; this highlights the additional sensitivity of $2W$ to the characteristic fluctuation rate Γ compared to the real part of the susceptibility. As the number of spins in a domain (argued in the finite-size hypothesis to go as $1/x^2$ [8]) increases, Γ will decrease; and, thus, the relaxation rate will increase with decreasing doping. Qualitatively, this is observed: $2W/T \sim C(x) \sim (1/x)^2$.

The detailed similarity of the magnetic properties of Sr- and Li-doped lanthanum cuprate cannot be understood in terms of individual holes interacting with impurities; this suggests that holes form collective structures. A full explanation of these magnetic properties cannot be given at this point, but to be concrete we propose a picture that can successfully account for the distinctive and complex behavior of Δ and $2W$ below T_N . Phase segregation of holes to boundaries of hole-free regions [8] or to hole-rich "rivers" [9] has been proposed. Based on the results of Tranquada *et al.* [13] at higher doping in $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$, we suggest a contrasting picture in which the stripes are density populated with holes (e.g., 1/2 hole per stripe Cu site) and constitute antiphase domain walls. We further suggest that these stripes close to form mobile loops that surround small domains (which we call antiphase domains) in the antiferromagnet. Such loops have been theoretically argued to be the stable configuration at low doping [19]. Because these encircling stripes are antiphase domain walls, the phase of the AF correlations in an antiphase domain is reversed with respect to the background. Motion of these domains (above 30 K) over a particular site thus reverses the spin orientation and reduces the time-averaged static moment at that site.

To estimate the size and density of domains required to explain experimental data, we consider a simple model [20] in which there is, on average, one domain for every N Cu sites (separated by lattice constant a). These N sites occupy an area $L^2 = Na^2$, and, of these, N_- sites compose the antiphase domain whose width is $l = a\sqrt{N_-}$. The fractional reduction of the time-averaged static moment at a given site will then be $(N_+ - N_-)/N$ where $N = N_+ + N_-$. We set this equal to $R(x) \equiv M_s^0(x)/M_s^0(x=0)$. Assuming 1/2 hole per Cu in the stripe, we have $4l \sim 2xNa$ (we assume that all donated holes are incorporated into loops), and $l/a \sim (1 - R)/x$. Using measured values of $R(y)$ for $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ [9], we find l/a increases with doping to ~ 20 at $y = 0.018$ where R has decreased to ~ 0.6 . Recovery of the sublattice magnetization below 30 K occurs when the domains either become pinned to the lattice or evaporate as the constituent holes become pinned to donor impurities. Mobile antiphase domains will introduce disorder and reduce the total interplane coupling of AF ordered regions thus reducing T_N [20].

In conclusion, we have presented a complete set of ^{139}La NQR data in lanthanum cuprate doped by in-plane

substitution of Li for Cu. The most striking result is the remarkable insensitivity of the magnetic properties of the AF CuO_2 planes to the nature and location of the dopant; this is in spite of marked differences in transport properties. This suggests the magnetic properties reflect collective hole phenomena. The behavior of $2W$ around T_N cannot be understood in the context of conventional critical behavior; we have demonstrated consistency with the finite-size scaling approach proposed earlier [8]. We propose that all of the data can be understood by means of a model in which doped holes segregate to domain walls that enclose mobile, antiphase bubbles which reduce the time-averaged ordered moment thus suppressing M_s^0 and T_N .

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