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Spin dynamics in $La_{2-x}Sr_xCuO_4$ ($0.02 \leq x \leq 0.08$) from ^{139}La NQR relaxation: Fluctuations in a finite-length-scale system

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^{139}La NQR spin-lattice relaxation rates (NSLR) versus temperature are presented for $La_{2-x}Sr_xCuO_4$ with $x=0.02$–0.08. The NSLR below $\sim 2T_N(x)$ shows a power-law critical behavior while above $\sim 2T_N(x)$ it follows an exponential law with a small x-dependent spin-stiffness constant, where $T_N(x)$ is the magnetic ordering temperature. It is argued that the NSLR arises from fluctuations of the staggered magnetization in locally ordered mesoscopic domains. We infer that the magnetically ordered state is not a conventional spin glass, as is often assumed.

The Cu^{2+} spin dynamics in the CuO_2 planes of $La_{2-x}Sr_xCuO_4$ mixed oxides has attracted a great deal of attention both because of the interest in two-dimensional (2D) model Heisenberg antiferromagnets (AF) and because of the possible connections of magnetic fluctuations with high-T_c superconductivity. The undoped parent compound La_2CuO_4 shows three-dimensional (3D) long-range AF order below $T_N \sim 300$ K. Upon doping, T_N is depressed rapidly with increasing x for $0 \leq x \leq 0.02$ and for $x > 0.02$ a magnetically ordered phase still appears at low temperatures. It has been argued that the latter magnetically ordered phase should be viewed as a disordered antiferromagnetic state as indicated by the presence of an internal magnetic field at the La site due to the ordered Cu moments[1] and a small anomaly in the specific heat.[2] The results of other experiments such as muon-spin-resonance[3,4] and muon-spin-relaxation (μSR) rate and quasielastic neutron scattering[5] have been found to resemble those of conventional spin glasses.

In addition, ^{139}La NQR relaxation rate (NSLR) measurements in $La_{2-x}Sr_xCuO_4$ with $x=0.01$, 0.025, and 0.05 indicated an enhancement of the NSLR as T approaches the magnetic ordering temperature $T_N \leq 10$ K.[6] The results were interpreted within the framework of dynamic scaling in terms of a slowing down of AF fluctuations due to the increase of the correlation length ξ with decreasing T resulting from localization of the mobile holes. However, recent inelastic neutron scattering results for $x=0.04$ fail to show localization effects and the consequent enhancement of the in-plane correlation length.[7] Rather, the neutron data are well described by a relation $\kappa(x,T)=\kappa(x,0)+\kappa(0,T)$ for the inverse correlation length, which implies a temperature-independent static spin-spin correlation length well below room temperature.

In this paper, we report complementary higher precision ^{139}La NQR NSLR data for carefully prepared samples, as a function of x and T in the intermediate doping regime of $La_{2-x}Sr_xCuO_4$ ($0.02 \leq x \leq 0.08$), together with an interpretation of these data which is consistent with the inelastic neutron scattering measurements. We argue that the NQR measurements probe the fluctuations among locally ordered mesoscopic domains and that the low-temperature ordered phase results from cooperative freezing of the staggered moments in the different domains. We infer that $La_{2-x}Sr_xCuO_4$ ($0.02 \leq x \leq 0.08$) is not a conventional spin glass as often assumed. Our results have important implications for the interpretation of a variety of other measurements of the magnetic properties of this system.

A series of powder samples of $La_{2-x}Sr_xCuO_4$ with composition from $x=0.02$ to $x=0.08$ was prepared using conventional ceramic techniques. The ^{139}La ($I=7/2$) NQR transition $5/2 \leftrightarrow 7/2$ was used to monitor the growth of magnetization towards its equilibrium value following a saturating radio frequency pulse sequence. The dominant relaxation mechanism for $T < 100$ K is due to fluctuations of the hyperfine field generated at the ^{139}La nucleus by the Cu^{2+} spins.[6] The magnetic relaxation transition probability W can be extracted from the multiexponential recovery of the echo amplitude. For a saturating sequence much shorter than W^{-1}, one can get the effective spin-lattice relaxation rate $R_1=23W$.[6]

The experimental results for R_1 vs T are shown in Fig. 1. The critical enhancement of R_1 near the ordering temperature T_N is accompanied by a divergence of the spin-spin relaxation rate and a consequent minimum in the echo signal intensity at T_N. The T_N values obtained from the minima in signal intensity are 10 K for $x=0.02$, 7.4 K for $x=0.03$, and 5.2 K for $x=0.04$, in good agreement with previous measurements.[2–4,6,8] In Fig. 2(a) it is shown that the temperature dependence of R_1 can be scaled, for all values of x and for $T_N(x) \lesssim T \leq 2T_N(x)$, to a power-law dependence $R_1 \propto \epsilon^{-n}=\{[T-T_N(x)]/T_N(x)\}^{-n}$ with $n=2.0 \pm 0.13$. As shown in Fig. 2(b), the

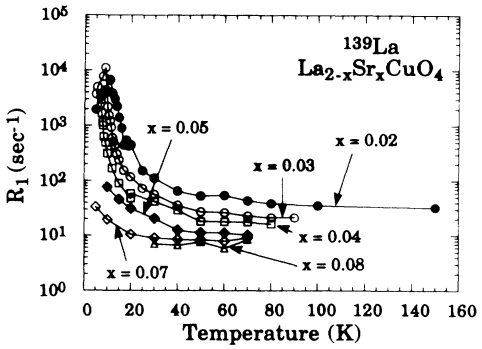

FIG. 1. The effective ^{139}La spin-lattice relaxation rate R_1 vs temperature for samples of $La_{2-x}Sr_xCuO_4$ with different x. The peak in the relaxation rate corresponds to the magnetic ordering temperature $T_N(x)$. The curves are guides to the eye.

temperature dependence of R_1 above $2T_N(x)$ can be fitted to an exponential behavior $R_1 = c(x)\exp[2J'(x)/T]$, with $c(x)$ and $2J'(x)$ given as a function of Sr doping x in Figs. 3(a) and 3(b), respectively. The previous ^{139}La NQR data[6] were not precise enough to resolve the different temperature dependences of R_1 in the two temperature regimes.

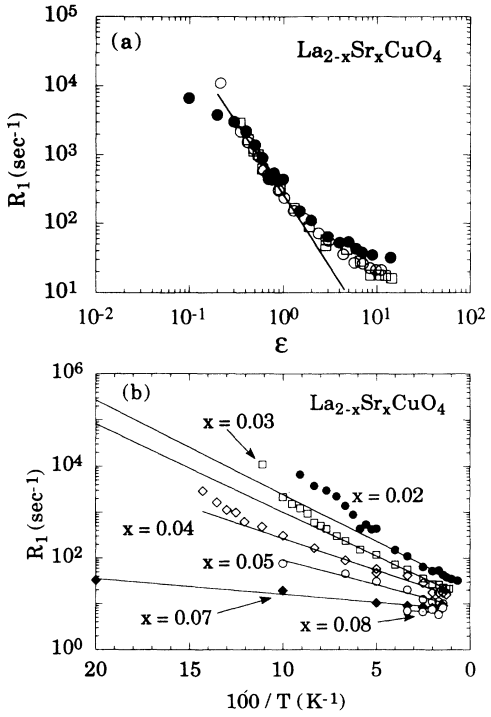

FIG. 2. (a) log-log plot of the ^{139}La spin-lattice relaxation rate R_1 above T_N from Fig. 1 vs $\epsilon \equiv [T - T_N(x)]/T_N(x)$, for $x = 0.02$, $T_N = 10$ K (●); $x = 0.03$, $T_N = 7.4$ K (○); $x = 0.04$, $T_N = 5.2$ K (□). The straight line corresponds to the common critical behavior $R_1 \propto \epsilon^{-2}$. (b) Semilogarithmic plot of R_1 vs inverse temperature $100/T$ for $La_{2-x}Sr_xCuO_4$ samples with different x. The lines are best fits of the expression $R_1 = c(x)\exp[2J'(x)/T]$ to the data above $\sim 2T_N(x)$. The departure of the experimental data from the fitting curves both in (a) and (b) occurs at the temperature of crossover between the exponential and the power-law behavior.

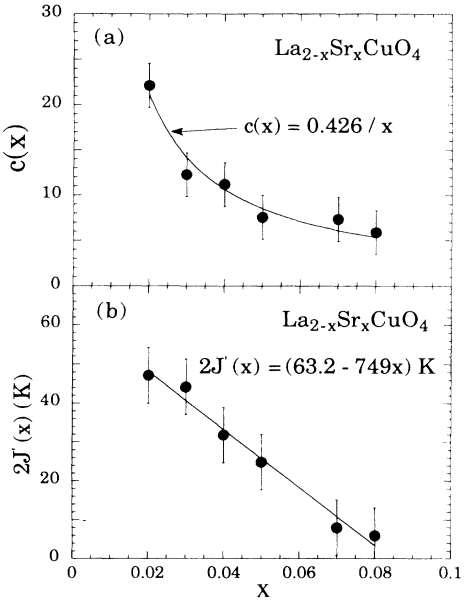

FIG. 3. Dependence on concentration x (a) of the constant $c(x)$ and (b) of the effective spin-stiffness constant $2J'(x)$ from the fits of the expression $R_1 = c(x)\exp(2J'(x)/T)$ to the data as shown in Fig. 2(b).

We begin our analysis of the ^{139}La NSLR data for $La_{2-x}Sr_xCuO_4$ by considering the case of undoped La_2CuO_4. This compound behaves as a 2D Heisenberg system with spin $S = \frac{1}{2}$, with important corrections to the magnetic correlation length ξ due to quantum effects[9]

$$\xi/a = C_\xi \exp(2\pi\rho_s/k_B T) , \tag{1}$$

where C_ξ is a constant of the order of unity, ρ_s is the spin-stiffness constant, and the AF exchange interaction between adjacent Cu spins is assumed to be of the form $H_{ij} = 2J\mathbf{S}_i \cdot \mathbf{S}_j$ ($2\pi\rho_s \simeq 2J > 0$). Due to the lack of inversion symmetry with respect to Cu^{2+} spins, ^{139}La nuclei couple rather effectively to AF fluctuations of these spins, mainly through dipolar terms. This is confirmed by the measured hyperfine field, $h_{\rm eff} = 1$ kG,[10] at the La site in the AF ordered phase.

For spin fluctuations faster than the quadrupole resonance frequency ω_Q, the relaxation transition probability is

$$2W = \tfrac{1}{2}\gamma_n^2 \int \langle h_+(0) h_-(t)\rangle dt = \gamma_n^2 \frac{1}{N} (h_{\rm eff})^2 \sum_q \frac{|S_q|^2}{\Gamma_q} , \tag{2}$$

where $\mathbf{h}(t)$ is the hyperfine field at the ^{139}La nucleus, isotropic fluctuations of the spin components S_q^α are assumed, and Γ_q is the decay rate of the collective spin fluctuations which are assumed to decay exponentially.[6] The far right-hand side of Eq. (2) is appropriate to describe critical effects dominated by the slowing down of a critical mode which couples to the nucleus considered. In this case, by using static and dynamic scaling arguments,[11] we can write $|S_q|^2 = \xi^{2-\eta} f(q\xi)$ and $\Gamma_q = \Gamma_c g(q\xi)$, where η is a critical exponent, ξ is in units of the lattice constant

a, and $f(q\xi)$, $g(q\xi)$ are homogeneous functions. By transforming the q summation into an integral ($\sum_q \rightarrow \int q^{d-1} dq$) and taking into account the convergence of $\int f(x)/g(x)dx$ to a number of the order of unity, one gets

$$R_1 = 23W = 11.5(\gamma_n h_{\text{eff}})^2 \xi^{2-d-\eta}/\Gamma_c = 11.5(\gamma_n h_{\text{eff}})^2 \xi^{z-\eta}/\omega_e . \quad (3)$$

Equation (3) should be valid for $d=2$ and in the presence of critical slowing down described by the dynamical scaling relation $\Gamma_c = \omega_e \xi^{-z}$, where z is a critical exponent. The coupling frequency $\omega_e = [8nJ^2 S(S+1)/3\hbar^2]^{1/2}$ corresponds to the value of Γ_c in the infinite temperature limit when no correlations are present. Here, $n=4$ is the number of nearest-neighbor magnetic ions.

In $Sr_2CuO_2Cl_2$, which contains layers of Cu^{2+} spins with about the same exchange coupling as in pure La_2CuO_4, the $\xi(T)$ extracted from Eq. (3) was found to agree with the theory [Eq. (1)] and neutron scattering results in La_2CuO_4,[12] except near T_N where a crossover to a power-law behavior of $\xi(T)$ is observed for $Sr_2CuO_2Cl_2$.[13] If we turn now to the doped $La_{2-x}Sr_xCuO_4$ system, we find that the enhancement of R_1 at low T (see Fig. 1) is clearly inconsistent with the temperature-independent ξ reported by neutron scattering[7] if one refers to Eq. (3). Therefore, we conclude that the dynamical scaling breaks down in the doped system $La_{2-x}Sr_xCuO_4$ ($0.02 \lesssim x \lesssim 0.08$), i.e., that critical effects dominated by the slowing down of a critical mode are not operative, and that the above description of the NSLR must be modified.

In considering alternative origins of our observed ^{139}La NSLR behavior in $La_{2-x}Sr_xCuO_4$, we first note that the correlation length ξ for undoped La_2CuO_4 is very large near and below room temperature: $\xi \gtrsim 10^2 - 10^3 a$, where a is the nearest-neighbor intraplanar Cu-Cu distance. Upon doping with Sr, the inelastic neutron scattering measurements demonstrated that well-defined 2D AF ordering is still present, but that ξ reaches an upper limit $\xi(T=0) \simeq a/\sqrt{x} \equiv L$ below ~ 300 K,[14] where $a \ll L \ll \xi$ for x in the range of interest here. In view of the failure of the above theory to predict our observed ^{139}La NSLR behavior, we therefore believe that the most likely alternative for the origin of this behavior is quasistatic ($\omega = \omega_Q \sim 0$) fluctuations of the staggered moments of the above *locally ordered* mesoscopic domains of size L.[15] To obtain a prediction for the ^{139}La NSLR from these fluctuations, we go back to Eq. (2) and write

$$R_1 = 23W = 11.5\gamma_n^2 \int \langle h_+(0) h_-(t) \rangle dt = 11.5\gamma_n^2 (h_{\text{eff}})^2/\Gamma_D , \quad (4)$$

where $(h_{\text{eff}})^2$ is the mean-square local hyperfine field and Γ_D is a characteristic frequency describing the relaxation of the staggered magnetization fluctuations within the domains. In writing Eq. (4), we assume that the hyperfine field h_{eff} is practically independent of L since it depends only on the first few Cu^{2+} nearest neighbors of a given ^{139}La nucleus. Furthermore, we assume $\Gamma_q = \Gamma_D$ (which implies that the local correlation time is dominated by the fluctuations of the staggered moment as a whole) and set the local mean-square normalized fluctuating moment $(1/N)\sum_q |S_q|^2 = 1$. By referring to the more widely used expression $R_1 \propto \lim_{\omega \rightarrow 0} \chi''(q,\omega)/\omega$, it is seen that Eq. (4) is consistent with the expression $\chi(q,\omega) \propto \xi^2 (1 + q^2\xi^2 - if)^{-1}$ and the proposed form $f = f(q\xi, qa, \omega/\Gamma, \omega/T)$ (Ref. 7) provided that, in the limit $\omega \rightarrow 0$, the dominant dependence is $f \propto \omega/\Gamma = \omega/\Gamma_D$ rather than $f \propto \omega/T$ as found in Ref. 7 for larger ω. By assuming in Eq. (4) $h_{\text{eff}} \simeq 1$ kG (Ref. 10) at the La site and $\omega_e \simeq 2.9 \times 10^{14}$ rad/sec estimated for $2J \simeq 1540$ K,[16] one can derive the x and T dependence of the correlation frequency Γ_D from the data analysis results in Figs. 2(a) and 3:

$$T_N(x) < T < 2T_N(x): \quad \frac{\omega_e}{\Gamma_D} = 500 \left(\frac{T - T_N(x)}{T_N(x)} \right)^{-2} , \quad (5a)$$

$$T > 2T_N(x): \quad \frac{\omega_e}{\Gamma_D} \equiv 1.81 c(x) \exp\left(\frac{2J'(x)}{T} \right) = \frac{0.78}{x} \exp\left(\frac{(63.2 - 749x)K}{T} \right) . \quad (5b)$$

The T dependence of Γ_D^{-1} in Eq. (5) is quite significant as it represents a direct measure of the slowing down of the thermodynamic fluctuations of the staggered magnetization in mesoscopic domains resulting from intradomain anisotropy and from the magnetic coupling of the domains to each other. The scaling of Γ_D vs x in $c(x)$ in Eq. (5b) should reflect the lifetime effect of the staggered moment. By generalizing the results in 1D magnets, where it is found that the lifetime of paramagnons is limited by the uncertainty in k vector due to finite-size correlation length,[17] one can argue that the lifetime Γ_D^{-1} should be proportional to the size L^d ($d=2$) of the locally ordered regions, leading to $\Gamma_D^{-1} \propto L^2 \propto x^{-1}$, as observed [Fig. 3(a), Eq. (5b)]. For $T > 2T_N(x)$, the fluctuations of the staggered moment appear to be determined by an effective spin-stiffness constant $2J'(x)$ which decreases with increasing x and goes to zero for $x \approx 0.08$ [Fig. 3(b), Eq. (5b)] in correspondence to the onset of the metallic and superconducting phase. This interpretation suggests that for $x \geq 0.08$, there is no transition into a magnetically ordered state at finite temperature. The exponential dependence of Γ_D^{-1} in Eq. (5b) is reminiscent of superparamagnetic relaxation in small magnetic particles.[18] By analogy, one could interpret $2J'(x)$ as arising from weak single ion anisotropy and average long-range dipolar terms coupling the domains, both terms being much smaller than the exchange constant $2J = 1540$ K [see Eq. (1)]. The resulting anisotropy, which acts as a barrier to the reorientation of the staggered moment, should scale as the number of spins in the domains and thus give the observed decrease of $2J'(x)$ with increasing x although the precise meaning of the linear x dependence (Fig. 3) and of the constant 62.3 K is hard to assess in absence of a detailed theory. The crossover to a power-law critical behavior of Γ_D observed for $T \rightarrow T_N(x)$ should then be ascribed to the cooperative behavior of the *correlated* finite-size regions, these being the entities that freeze in the magnetically ordered phase; this phase is thus *not* a conventional spin glass as often assumed.

In conclusion, the present interpretation removes inconsistencies between NQR and inelastic neutron scattering[7] results for $La_{2-x}Sr_xCuO_4$ ($0.02 \lesssim x \lesssim 0.08$) by showing the complementary nature of the two measurements; whereas the former measurement is sensitive mainly to the local quasielastic fluctuations of the order parameter within mesoscopic domains which are affected by the coupling between domains, in the latter technique one probes also the high-frequency spin-wave-like excitations within one domain. In this respect NMR/NQR should not be unique in probing the superparamagnetic fluctuations in regions of finite size, i.e., far smaller than the thermodynamic correlation length ξ; analysis of other low-frequency measurements on $La_{2-x}Sr_xCuO_4$ ($0.02 \lesssim x \lesssim 0.1$) like μSR and quasielastic neutron scattering[3-5] will be important in testing our interpretation.[19] Consideration of finite-size effects as documented here may resolve other unexplained phenomena such as the anomalously strong depression of the 3D AF ordering temperature T_N and the rapid decrease of the ordered Cu moment with x in $La_{2-x}Sr_xCuO_4$ for $0 \leq x \leq 0.02$.[20] Indeed, from careful measurements of samples with $0 \leq x \leq 0.02$, T_N is found to follow a power-law dependence on x, consistent with the finite-size-scaling hypothesis,[20] which lends independent support to our interpretation.

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[1] Y. Kitaoka *et al.*, Physica C **153-155**, 733 (1988).
[2] S. Aldrovandi *et al.*, J. Appl. Phys. **67**, 5052 (1990).
[3] D. R. Harshmann *et al.*, Phys. Rev. B **38**, 852 (1988).
[4] J. I. Budnick *et al.*, Europhys. Lett. **5**, 651 (1988).
[5] B. J. Sternlieb *et al.*, Phys. Rev. B **41**, 8866 (1990).
[6] F. Borsa *et al.*, Nuovo Cimento D **11**, 1785 (1989); A. Rigamonti *et al.*, in *Earlier and Recent Aspects of Superconductivity,* edited by J. G. Bednorz and K. A. Müller (Springer, Berlin, 1990).
[7] B. Keimer *et al.*, Phys. Rev. Lett. **67**, 1930 (1991).
[8] I. Watanabe *et al.*, J. Phys. Soc. Jpn. **56**, 3028 (1987).
[9] S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **60**, 1057 (1988); Phys. Rev. B **39**, 2344 (1989).
[10] H. Nishihara *et al.*, J. Phys. Soc. Jpn. **56**, 4559 (1987).
[11] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
[12] Y. Endoh *et al.*, Phys. Rev. B **37**, 7443 (1988); K. Yamada *et al.*, *ibid.* **40**, 4557 (1989).
[13] F. Borsa, M. Corti, T. Goto, A. Rigamonti, D. C. Johnston, and F. C. Chou, Phys. Rev. B **45**, 5756 (1992).
[14] R. J. Birgeneau *et al.*, Phys. Rev. B **39**, 2868 (1989).
[15] S. Chakravarty, Phys. Rev. Lett. **66**, 481 (1991).
[16] G. Aeppli *et al.*, Phys. Rev. Lett. **62**, 2059 (1989).
[17] M. Steiner, J. Villain, and C. G. Windsor, Adv. Phys. **25**, 87 (1976).
[18] See, for example, G. Xiao *et al.*, Phys. Rev. B **34**, 7573 (1986).
[19] If the maximum in the neutron scattering 2D integrated intensity in Ref. 7, observed at about 75 K for the lowest energy investigated (4.5 meV), were to be attributed entirely to the quasielastic fluctuations of the mesoscopic domains one would expect $\Gamma_D \simeq 4.5$ meV $= 6.8 \times 10^{12}$ rad/sec at $T = 75$ K in good agreement with Eq. (5b) which yields $\Gamma_D = 9.5 \times 10^{12}$ rad/sec (for $x = 0.04$).
[20] J. H. Cho, F. C. Chou, and D. C. Johnston, Bull. Am. Phys. Soc. **37** (1), 231 (1992); and (unpublished).