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Spin dynamics in hole-doped two-dimensional S = 1/2 Heisenberg antiferromagnets: ^{63}Cu NQR relaxation in $La_{2-x}Sr_xCuO_4$ for $x \leq 0.04$

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Abstract. The effects on the correlated Cu^{2+} $S = 1/2$ spin dynamics in the paramagnetic phase of $La_{2-x}Sr_xCuO_4$ (for $x \lesssim 0.04$) due to the injection of holes are studied by means of ^{63}Cu NQR spin-lattice relaxation time T_1 measurements. The results are discussed in the framework of the connection between T_1 and the in-plane magnetic correlation length $\xi_{2D}(x,T)$. It is found that at high temperatures the system remains in the renormalized classical regime, with a spin stiffness constant $\rho_s(x)$ reduced by small doping to an extent larger than the one due to Zn doping. For $x \gtrsim 0.02$ the effect of doping on $\rho_s(x)$ appears to level off. The values for $\rho_s(x)$ derived from T_1 for $T \gtrsim 500$ K are much larger than the ones estimated from the temperature behavior of sublattice magnetization in the ordered phase ($T \leq T_N$). It is argued that these features are consistent with the hypothesis of formation of stripes of microsegregated holes.

PACS. 76.60.-k Nuclear magnetic resonance and relaxation – 74.20.Mn Nonconventional mechanisms (spin fluctuations, polarons and bipolarons, resonating valence bond model, anyon mechanism, marginal Fermi liquid, Luttinger liquid, etc.) – 75.40.Gb Dynamic properties (dynamic susceptibility, spin waves, spin diffusion, dynamic scaling, etc.)

Besides being the parent compound of high temperature superconductors, La_2CuO_4 can be considered as a prototype for the investigation of quantum spin magnetism in planar square lattice Heisenberg antiferromagnets (2D-QHAF) [1,2]. This compound shows, over a wide temperature range, $T_N \simeq 315\,\mathrm{K} < T < J \simeq 1500\,\mathrm{K}$, strong in-plane correlations without 3D long range order. Recent theories for 2D-QHAF [3,4] predict that La_2CuO_4 above T_N is in the renormalized classical (RC) regime, where the spin wave stiffness ρ_s and the spin wave velocity c_{sw} are renormalized by quantum fluctuations with respect to the correspondent classical mean field values. In the RC regime one expects for the in-plane magnetic correlation length [4]

$$\xi_{2D}/a = \frac{\hbar c_{sw}}{16\pi k_B \rho_s} e^{\frac{2\pi\rho_s}{T}}\left[1 - 0.5\frac{T}{2\pi\rho_s}\right]$$
$$= 0.493 e^{1.15J/T}\left[1 - 0.43\frac{T}{J} + O(\frac{T}{J})^2\right] \qquad (1)$$

where a is the lattice constant. The spin stiffness constant has been written $\rho_s = 1.15J/2\pi$, while $c_{sw} = 1.18\sqrt{2}Jk_B/\hbar$, with J in temperature units.

Recently [5,6], from a series of ^{63}Cu and ^{139}La NQR and μSR measurements in spin-doped La_2CuO_4, where Cu^{2+} ions were substituted by $Zn^{2+}(S = 0)$ ions, several aspects have been clarified: (i) the pure La_2CuO_4 remains in the RC regime up to $T \simeq 900$ K. (ii) The values for ξ_{2D} derived from ^{63}Cu NQR relaxation rates are in close quantitative agreement with those derived from neutron scattering. (iii) Above 900 K a possible crossover to a quantum critical (QC) regime occurs. (iv) The effect of Zn-doping on ξ_{2D} in the RC regime can be satisfactory described in terms of a dilution-like model, whereby the doping causes a decrease of the spin stiffness of the form $\rho_s(x) = \rho_s(0)[1 - (2 - x)x]$. (v) Up to $\simeq 800$ K there is no evidence of a crossover to a QC regime, even for Zn doping levels up to 11%. On the other hand, the effects of heterovalent (Sr^{2+} for La^{3+}) substitutions, where itinerant holes coupled in singlet states with Cu^{2+} spins perturb the 2D antiferromagnetic (AF) correlation, have not been entirely clarified yet. The problem of the effects of charge doping on the magnetic properties of the CuO_2 plane is of particular interest. In fact, besides causing the drastic

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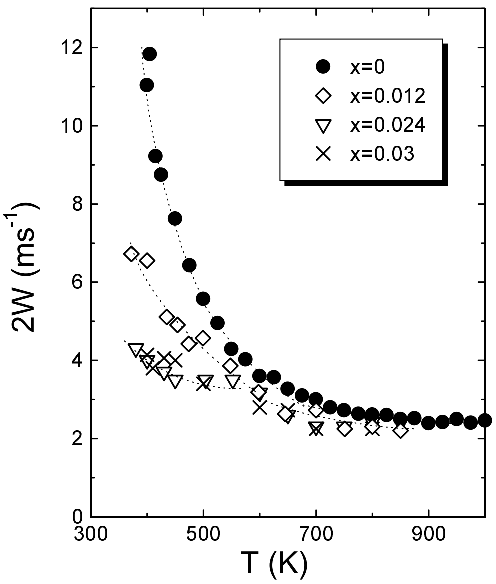

Fig. 1. ^{63}Cu NQR spin-lattice relaxation rates $2W$ in the paramagnetic phase of $La_{2-x}Sr_xCuO_4$ for different Sr doping levels x. The lines are guides to the eye.

decrease of the Néel temperature with doping ($T_N \to 0$ at $x = x_c = 0.02$) [7,8] the role of the itinerant charges is relevant for the mechanisms underlying high T_c superconductivity, particularly in the light of the theoretical approaches based on the microscopic segregation of the itinerant holes along stripes [2,9,10]. In this report ^{63}Cu NQR spin-lattice relaxation measurements in the doping range just below and just above the critical concentration $x_c = 0.02$ are presented. It is argued how some evidence for the presence of dynamical charge separation in domain walls is provided by the data.

Single phase samples of $La_{2-x}Sr_xCuO_4$ were prepared by solid state reaction and annealed in 1 bar O_2 [7,8,11]. Oxygen exchange during the high temperature measurements was prevented by sealing the samples in pyrex ampoules. The ^{63}Cu NQR frequency is in the range 33−33.5 MHz depending on the composition of the sample. ^{63}Cu relaxation rates have been obtained with a pulse spectrometer by monitoring the recovery of the echo amplitude after a sequence of pulses yielding equalization of the populations of the $\pm 1/2$ and $\pm 3/2$ ^{63}Cu NQR levels. The relaxation rate was extracted from the exponential recovery of the echo intensity. The experimental results for 2W as a function of temperature are shown in Figure 1 for some samples with different concentrations x of Sr dopant. Our results for $x = 0.04$, not shown in Figure 1, agree with the ones reported previously for the same concentration by other authors [12]. The enhancement of the relaxation rate as the temperature is lowered becomes less pronounced as the concentration of Sr increases. In all the samples investigated the NQR signal is lost well above the antiferromagnetic transition temperature T_N due to the progressive decrease of the echo dephasing time T_2 on decreasing temperature [5].

^{63}Cu nuclear spin-lattice relaxation in La_2CuO_4 is driven by the magnetic field fluctuations at the nuclear site and one can write

$$1/T_1 \equiv 2W = \frac{\gamma^2}{2} \int_{-\infty}^{+\infty} \mathrm{e}^{-\mathrm{i}\omega_R t} \langle h_-(0) h_+(t) \rangle \mathrm{d}t \qquad (2)$$

where γ is the ^{63}Cu gyromagnetic ratio, ω_R is the resonance frequency and $h_\pm$ are the components of the fluctuating field transverse to the quantization axis (the c-axis, corresponding to the direction of the V_{zz} electric field gradient component). The hyperfine field at the Cu nucleus can be written $\mathbf{h} = \mathcal{A}\mathbf{S}_o + \sum_{i=1}^{4} B\mathbf{S}_i$, where the on-site interaction constant is $A_\perp = 80$ kGauss, while the transferred hyperfine coupling constant is $B = 83$ kGauss [13]. From the correlation function $\langle h_+(0) h_-(t) \rangle$ in equation (3) one arrives at $2W = (\gamma^2/2) \sum_{\mathbf{q}} \mathcal{A}_{\mathbf{q}}^2 |S_{\mathbf{q}}|^2 / \Gamma_{\mathbf{q}}$, where $|S_{\mathbf{q}}|^2$ is the amplitude of the collective spin fluctuations, and $\Gamma_{\mathbf{q}}^{-1}$ the corresponding decay time. The coupling constant is $\mathcal{A}_{\mathbf{q}}^2 = [A_\perp - 2B(\cos(q_x a) + \cos(q_y b))]^2$, with $\mathbf{q}$ starting from $(\pi/a, \pi/a)$ [13]. Since in the temperature range of interest $\xi_{2D} \gg a$, scaling arguments for $|S_{\mathbf{q}}|^2$ and $\Gamma_{\mathbf{q}}$, or equivalently for the generalized susceptibility $\chi(\mathbf{q}, \omega)$, can be used. Then $\chi(\mathbf{q}, \omega) = \chi_o \xi^z f(q\xi, \omega/\xi^z)$, with $\chi_o = S(S+1)/3k_B T$ and z the dynamical scaling exponent, and one obtains [5]

$$2W = \gamma^2 \frac{S(S+1)}{3} \epsilon \left(\frac{\xi_{2D}}{a}\right)^{z+2} \frac{\beta^2 \sqrt{2\pi}}{\omega_e} \left(\frac{a^2}{4\pi^2}\right) \times \int_{BZ} \mathrm{d}\mathbf{q} \frac{[A_\perp - 2B(\cos(q_x a) + \cos(q_y b))]^2}{(1 + q^2 \xi_{2D}^2)^2} \qquad (3)$$

where ω_e is the Heisenberg exchange frequency describing the fluctuations in the limit of infinite temperature, $\epsilon = 0.3$ takes into account the reduction of the amplitude due to quantum fluctuations [3,14] and β is a normalization factor preserving the total moment sum rule. It is noted that a simple analytical form emphasizing the connections of ξ_{2D} to $2W$ can be obtained by averaging over the Brillouin zone the form factor in square brackets of equation (3). In this case $2W \simeq 4.2 \times 10^3 (\xi_{2D}/a)^z / [\ln(q_m \xi_{2D})]^2 \, \mathrm{s}^{-1}$, where $q_m = 2\sqrt{\pi}/a$ (see Ref. [5]).

The validity of equation (3) was found [5,6] to extend up to temperatures $T = 1000$ K for La_2CuO_4, where $\xi_{2D}/a \simeq 2$. Therefore it could be argued that for low dimensional systems the validity of scaling arguments is not strictly limited to the range where $\xi_{2D}/a \gg 1$. In this respect it is worth pointing out that the maximum in the magnetic susceptibility, which indicates the occurrence of substantial short range order, is estimated for La_2CuO_4 around 1500 K [2], where $\xi_{2D}/a \simeq 1$. Therefore, one can safely use equation (3), with a numerical integration over the Brillouin zone, to extract, from the experimental evaluation of T_1, the temperature and doping dependence of $\xi_{2D}(x, T)$. The results are shown in Figure 2, for different Sr concentrations. The slope of the semilog plot of ξ_{2D} *vs.* $1000/T$ decreases with increasing Sr concentration, reflecting the decrease of the spin stiffness $\rho_s(x)$ in equation (1).

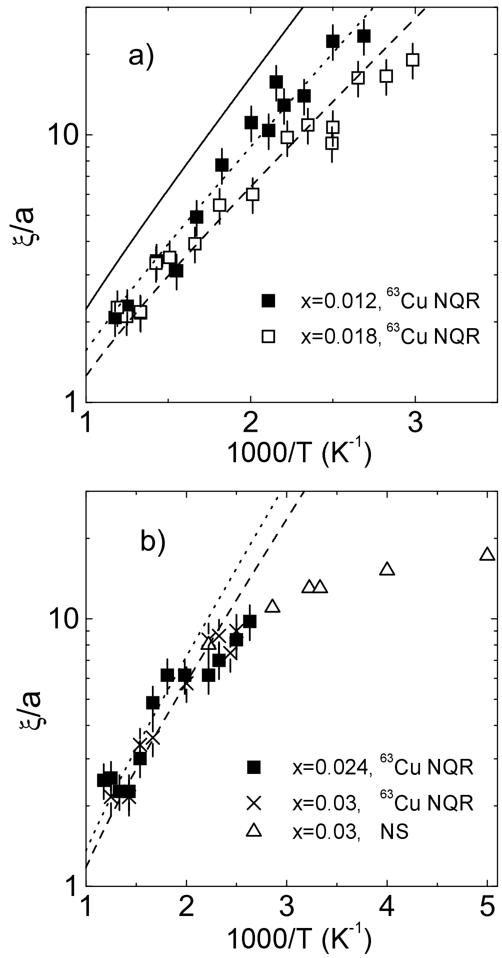

Fig. 2. In-plane magnetic correlation length ξ_{2D} as a function of inverse temperature in the paramagnetic phase of $La_{2-x}Sr_xCuO_4$, as extracted from ^{63}Cu NQR spin-lattice relaxation rate measurements (see text) for (a) $x < 0.02$ and (b) $x > 0.02$. The dotted and dashed lines are best fits according to equation (1) with values of $J(x)$ as follows: $J(0.012) = 1340$ K, $J(0.018) = 1200$ K, $J(0.024) = 1250$ K, $J(0.03) = 1160$ K. In (a) the solid line shows the corresponding behavior of ξ_{2D} for $x = 0$, where $J = 1588$ K. In (b) the triangles show the data for $x = 0.03$ obtained from neutron scattering (Ref. [15]).

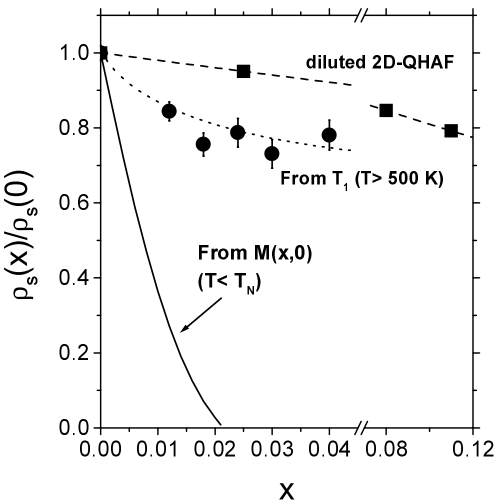

Fig. 3. Concentration x dependence of the spin-stiffness $\rho_s(x)/\rho_s(0) \propto J(x)/J(0)$ in $La_{2-x}Sr_xCuO_4$ as derived form the fits in Figure 2 (solid circles, the dotted line is a guide to the eye). The dashed line represents the behavior of $\rho_s(x)/\rho_s(0)$ for a diluted 2D-QHAF, while the squares show the corresponding values derived from $1/T_1$ in Zn-doped La_2CuO_4 (see Ref. [5]). The solid line shows the behavior for $\rho_s(x)/\rho_s(0)$ derived on the basis of the analysis of the magnetization data (Ref. [14]) by Castro Neto and Hone (Ref. [17]) (see text).

For $x \lesssim 0.02$ the data can be fitted over all the explored temperature range by using equation (1), with $J = 1340$ K (± 40 K) for $x = 0.012$ and $J = 1200$ K (± 50 K) for $x = 0.018$ respectively. The decrease of the spin stiffness with x, for $x \to 0$, is faster than expected for a diluted 2D AF, as Zn-doped La_2CuO_4 [5] (see Fig. 3). The more pronounced decrease of the spin-stiffness for Sr^{2+} doping should be associated with the mobile nature of the holes which induce a larger damping in the spin excitations [16,17]. On the other hand it can be observed that the decrease of the spin-stiffness with x is weaker than the one derived for holes randomly itinerating in the AF matrix, namely $\rho_s(x) \propto 1/x$ [16,17]. From this observation one is lead to conjecture that a reduced effective amount of holes controls the spin stiffness for $x \gtrsim 0.015$. A reduction in the local carrier density could in principle result from the microsegregation of the hole carriers along stripes (or segments of stripes) which leave a hole depleted region in between them. Within this line of interpretation one would conclude that $La_{2-x}Sr_xCuO_4$ remains in the RC regime with a spin-stiffness constant reduced with respect to the pure La_2CuO_4, up to the limit where the correlation length is smaller than the average distance l between stripes.

For large doping the increase in T_2 allows one to extend $1/T_1$ measurements at lower temperatures. For $T \gtrsim 550$ K even for $x \geq 0.02$ $La_{2-x}Sr_xCuO_4$ remains in the RC regime. However, below about 550 K, for $x \gtrsim 0.02$, one has a flattening in the T dependence of ξ_{2D}. The tendency of ξ_{2D} towards saturation has been already observed through neutron scattering measurements by Keimer *et al.* [15] and described on the basis of the phenomenological expression $1/\xi(x,T) = 1/\xi(x,0) + 1/\xi(0,T)$, where $\xi(0,T)$ is given by equation (1) with $J = 1588$ K. The x dependence of the correlation length for $T \to 0$ yields information on the topology of the holes. If the holes are localized close to the randomly distributed Sr^{2+} impurity ions, one expects $\xi(x,0) = a/\sqrt{x} = 3.8/\sqrt{x}$ Å [18]. On the other hand, if the correlation length is limited by the formation of domain walls where the mobile holes are segregated, then $\xi(x,0) = a/nx$, where n is the average distance between the holes along the domain walls in lattice units [19,20]. Although it is difficult to distinguish the x dependence of the form $1/x$ from the $1/\sqrt{x}$ one, it should be noticed that the estimated values of $\xi(x,0)$ do confirm the microsegregation. In fact, the assumption of a random distribution of holes would imply values for $\xi(x,0)$ much smaller than the ones experimentally measured. For example, for $x = 0.03$ one should have $\xi(x,0) = a/\sqrt{x} \simeq 6a$, while the experimental value is $\xi(x,0) \simeq 20a$ (see Fig. 2). On the contrary, in the presence of stripes, with $n = 2$ (as found by Tranquada *et al.* [20] in the $x = 1/8$ compound), one obtains $\xi(x = 0.03, 0) \simeq 16a$, in close agreement with the experimental finding.

Also these estimates appear to reinforce the idea that the holes segregate along domain walls, or stripes. The occurrence of the stripes was originally proposed in order to justify the susceptibility [7] and the x dependence of the sublattice magnetization $M(x,0)$ in the limit $T \to 0$, as derived from ^{139}La NQR and μSR measurements [19]. A quantitative description of the effective spin stiffness $\rho_s(x)$ resulting from the presence of the stripes below T_N has been given by Castro Neto and Hone [21] and more recently by van Duin and Zaanen [22]. These descriptions are based on the quantum non-linear σ model and assume an in-plane anisotropy for the superexchange constant J in an effective Heisenberg Hamiltonian. In this framework, for $T \to 0$ a pronounced decrease of the spin stiffness with x justifies the experimental behavior for $M(x,0)$ [19].

It is worth to compare the x-dependence of $\rho_s(x)$ derived in the high temperature range from ^{63}Cu NQR T_1 (Fig. 3) with the behavior for $\rho_s(x)$ expected at low temperature on the basis of the picture by Castro Neto and Hone [21]. In Figure 3 the solid line shows the x-dependence of the spin stiffness according to equation (7) in reference [21]. The comparison with the data for $\rho_s(x)$ derived from ^{63}Cu NQR T_1 shows that the decrease of $\rho_s(x)$ from T_1 is much smaller than the one derived from the staggered magnetization. The difference is related to the different temperature regions probed by the two quantities, implying that two different regimes are present in the spin dynamics. At high temperature, where $\xi_{2D} < l$, the stripes are mobile, possibly corresponding to antiphase boundaries [21] and the spin excitations are the ones characteristic of the 2DQHAF with a reduced number of holes. Accordingly, $\rho_s(x)$ is only slightly reduced by doping. The characteristic fluctuation time for the stripes is much longer than ω_e^{-1} and in the life time of the spin excitations the stripes appear as nearly static. On the contrary, in the low temperature regime, where $\xi_{2D} > l$, the stripes reduce the effective superexchange coupling perpendicular to the domain walls and cause the pronounced decrease of the spin-stiffness constant. Since no narrowing in the ^{139}La NQR spectra has been observed [19], one can conclude that the hopping rate for the stripes should be lower than $\simeq 100$ kHz, for $T \leq T_N$. In between these two regimes ξ_{2D} is of the order of l and one observes a progressive saturation of ξ_{2D} on decreasing temperature (corresponding to a reduction of ρ_s).

In conclusion the ^{63}Cu NQR $1/T_1$ measurements in lightly doped $La_{2-x}Sr_xCuO_4$ evidence that the spin-stiffness constant at high temperatures is reduced by doping only to a small extent, consistent with the idea of formation of stripes. On decreasing temperature a progressive saturation for the in-plane correlation length is found, with a concomitant decrease in the spin-stiffness. The temperature dependence of ρ_s and the analysis of the correlation length $\xi_{2D}(x,T)$ support the hypothesis of microsegregation of the holes along stripes.

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