RAPID COMMUNICATIONS

Spin dynamics in the low-temperature tetragonal phase of $\cong\frac{1}{8}$ doped single crystal $La_{1.67}Eu_{0.2}Sr_{0.13}CuO_4$

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We present ^{139}La and ^{63}Cu NMR relaxation measurements in single crystal $La_{1.67}Eu_{0.2}Sr_{0.13}CuO_4$. A strong peak in the ^{139}La spin-lattice relaxation rate observed in the spin ordered state is well described by the BPP mechanism [Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948)] and arises from continuous slowing of electronic spin fluctuations with decreasing temperature; these spin fluctuations exhibit XY-like anisotropy in the ordered state. The spin pseudogap is significantly enhanced by the static charge-stripe order in the LTT phase.

Understanding spin dynamics and correlations in high-temperature superconductors (HTSC's) is crucial to solving the mechanism of the superconductivity. The existence of low-frequency antiferromagnetic (AF) spin fluctuations in the CuO_2 planes and the opening of a spin pseudogap in the normal state are two poorly understood features of HTSC.[1,2] An anomalous suppression of T_c is observed for a hole concentration of 1/8 in $La_{2-x}Ba_xCuO_4$ and for a range of hole concentrations near this value in rare-earth co-doped $La_{2-x-y}M_ySr_xCuO_4$(M=Eu, Nd);[3,4] in both cases a structural phase transition (SPT) to the low-temperature tetragonal (LTT) phase occurs. The observation of incommensurate elastic neutron-diffraction peaks indicative of static charge stripe order in the LTT phase of $La_{2-x-y}Nd_ySr_xCuO_4$ (Ref. 5) followed by incommensurate magnetic order indicates that spin order is induced by the charge stripe order[5] and emphasizes the importance of understanding the magnetism in these charge stripe ordered systems.

Incommensurate magnetic peaks have also been observed near ~30 K in Eu co-doped compounds by elastic neutron scattering[6] revealing static stripe order, and muon spin rotation (μSR) studies confirm magnetic order in Nd and Eu compounds below ~30 K.[7–9] μSR studies of the Nd material find a lower magnetic ordering temperature indicating quasistatic magnetic behavior, and Tranquada *et al.* have argued that the magnetic order is glassy.[10] Electron-spin-resonance (ESR) studies in a series of $La_{2-x-y}Eu_ySr_xCuO_4$ samples[11] have associated this ordering with continuous slowing of spin fluctuations with decreasing temperature.

We have investigated the spin dynamics of $x\cong 1/8$ doped $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ using nuclear magnetic resonance (NMR) to better understand the influence of charge stripes on the quasistatic spin order. We report a strong peak in the ^{139}La spin-lattice relaxation rate $^{139}T_1^{-1}$ below the spin ordering temperature (see Fig. 1), a remarkable situation quite similar to AF ordered lanthanum cuprate with an order of magnitude smaller doping.[12–14] The frequency dependence of this peak is well explained by a mechanism first discussed by Bloembergen, Purcell, and Pound (BPP): ^{139}La relaxation

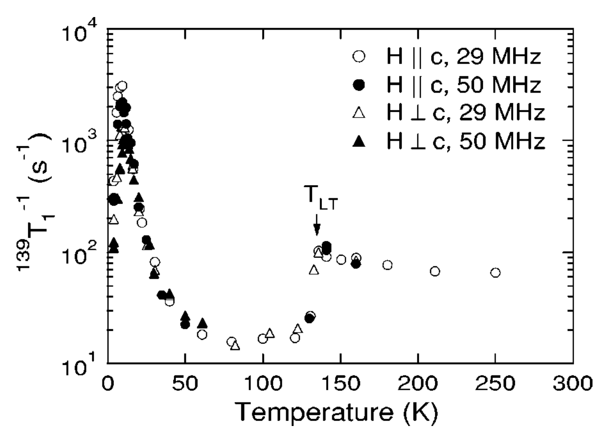

FIG. 1. The lanthanum spin-lattice relaxation rate $^{139}T_1^{-1}$ in single crystal $La_{1.67}Eu_{0.2}Sr_{0.13}CuO_4$ measured in two applied fields (ν=29 and 50 MHz) is shown for two orientations of the field (**H**) with respect to the crystal c-axis.

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is due electronic spin fluctuations whose characteristic rate τ_c^{-1} slows with decreasing temperature, and the peak occurs (at $T=T_f\sim 9$ K) when τ_c^{-1} matches the NMR frequency (30–50 MHz). Our measurements also reveal a very strong orientation dependence of $^{139}T_1^{-1}$ in the vicinity of the peak demonstrating a strong anisotropy of the spin fluctuations in the ordered state similar to those observed in XY-like systems. $^{139}T_1^{-1}$ also exhibits an abrupt decrease at $T_{\rm LT}$. ^{63}Cu spin-lattice and spin-spin relaxation measurements reveal a spin pseudogap significantly more pronounced than occurs in similarly doped $La_{2-x}Sr_xCuO_4$ indicating that static charge stripes in the LTT phase significantly enhance the spin pseudogap.

Our ^{139}La and ^{63}Cu NMR relaxation measurements were performed on a $La_{1.67}Eu_{0.2}Sr_{0.13}CuO_4$ single crystal that undergoes the low-temperature orthorhombic (LTO) $\rightarrow$LTT SPT at $T=134\pm 2$ K. The crystal was grown using the traveling solvent floating zone method under oxygen pressure of 3 bar.[15] From dc magnetization measurements, no superconducting transition is observed down to 4.2 K. Static spin order is observed below $\approx$20 K in μSR studies.[9] Both the ^{139}La ($I=7/2$) and ^{63}Cu ($I=3/2$) spin-lattice relaxation rates were measured by monitoring the recovery of the central transition ($m_I=+1/2\leftrightarrow -1/2$) magnetization after saturation with a single $\pi/2$ pulse. The ^{63}Cu spin-spin relaxation was measured by monitoring the spin-echo decay using a two-pulse Hahn-echo ($\pi/2-\tau-\pi$). The time dependence of the magnetization recovery does not conform to the standard theoretical expression[16] over the entire temperature range investigated. Far above $T_{\rm LT}$ and in the intermediate range $30 \lesssim T \lesssim T_{\rm LT}$, the data were well fit by this expression for magnetic relaxation and saturation by a single pulse,[16] however around $T_{\rm LT}$ and at low T ($\lesssim$30 K), this fit is poorer. We ascribe the slight deviation around $T_{\rm LT}$ to the additional motion of oxygen octahedra associated with the SPT; this generates a quadrupolar contribution to the ^{139}La relaxation.[17] As in lightly doped La214,[12,14,17] stretched exponential recoveries are observed at low T.

To provide a consistent basis for analysis of the T dependence of $^{139}T_1^{-1}$, the first decade of recovery data was fit, for all T, to the stretched exponential function $[M(\infty)-M(t)]/M(\infty)=\exp[-(t/T_1)^{1/2}]$. While this analysis increases the uncertainty in $^{139}T_1^{-1}$ for $T\gtrsim 30$ K, we find that varying the fitting procedure has essentially no effect on the behavior at $T_{\rm LT}$.

The T dependencies of $(^{63}T_1T)^{-1}$ and $^{63}T_{2G}^{-1}$ are shown in Fig. 2. The ^{63}Cu magnetization recovery data for whole temperature range investigated are well fit by the theoretical expression[16] for magnetic relaxation following single pulse saturation: $[M(\infty)-M(t)]/M(\infty)=0.1\exp(-t/T_1)+0.9\exp(-6t/T_1)$. $^{63}T_{2G}^{-1}$ was obtained by fitting the spin-echo amplitude, $S(t=2\tau)$, to the expression: $S(t)=S(0)\exp(-t/T_{2R})\exp[-(t/T_{2G})^2/2]$. The contribution of spin-lattice relaxation processes to the spin-echo decay, T_{2R}^{-1}, was determined from $T_{2R}^{-1}=(\beta+R)/^{63}T_1$ with $\beta=3$ and the anisotropy of $^{63}T_1^{-1}$, $R=3.6$.[18] Because we cannot entirely invert the Cu line these T_{2R}^{-1} data are not quantitatively accurate, but they reliably indicate the qualitative T dependence of T_{2R}^{-1}. The ^{63}Cu NMR linewidth (full width at half maximum) $\Delta H\simeq 1.2$ kG at $T=240$ K, and is observed to

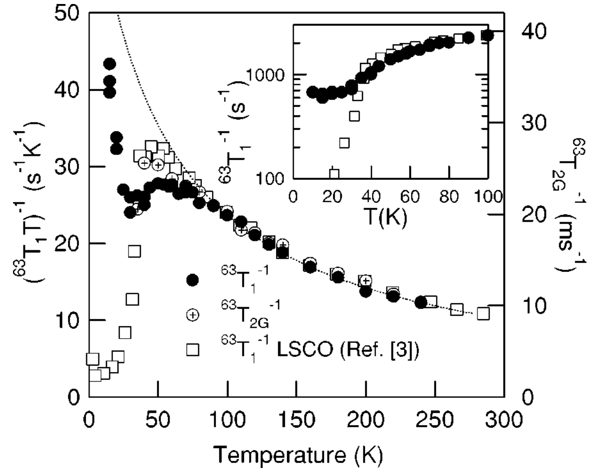

FIG. 2. Copper spin-lattice relaxation: the T dependencies of $(^{63}T_1T)^{-1}$ and $^{63}T_{2G}^{-1}$ measured in an applied field ($\nu=90$ MHz) are shown for $\mathbf{H}\| c$ axis; $(^{63}T_1T)^{-1}$ for identically doped $La_{1.87}Sr_{0.13}CuO_4$ (Ref. 2) is also shown for comparison. The solid curve is a Curie-Weiss law fit for $T\geqslant 100$ K: $(^{63}T_1T)^{-1}\propto 1/(T+\theta)$ with $\theta=16$ K. Inset: A semilog plot of $^{63}T_1^{-1}$ vs T.

increase monotonically to $\simeq$3.4 kG at $T=40$ K. Consistent with earlier work we observe a strong suppression of the intensity of the ^{63}Cu NMR signal with decreasing T;[19] this suppression is well explained by the slow electron-spin fluctuations responsible for the low-T peak in $^{139}T_1^{-1}$.[20]

In our discussion we will focus on the following: (i) characterizing the LTO$\rightarrow$LTT SPT, (ii) demonstrating that the low-T spin-freezing peak in $^{139}T_1^{-1}$ is well described by the BPP mechanism[21] which reveals that the low-T spin dynamics are characterized by a *distribution* activation energies, $E_a/k_B\sim 100$ K, and (iii) $^{63}T_1^{-1}$; particularly the contrast with $x=1/8$, LTO-phase superconducting $La_{2-x}Sr_xCuO_4$.

The abrupt decrease in $^{139}T_1^{-1}$ at $T_{\rm LT}$ with essentially no enhancement above $T_{\rm LT}$ contrasts with the behavior of lightly doped $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$, where a strong enhancement is observed above $T_{\rm LT}$.[17] This result is consistent with the observation that the LTO$\rightarrow$LTT SPT in this heavily doped sample is first order.[22,23]

The strong orientation and frequency dependencies of the low-T peak in $^{139}T_1^{-1}$ evident in Fig. 3 clearly indicate that it results from continuous slowing of anisotropic spin fluctuations with decreasing T. The same frequency dependence of $^{139}T_1^{-1}$ below T_f is observed by comparing different nuclear quadrupole resonance (NQR) transitions in zero field, hence the frequency dependence does not reflect a magnetic-field dependence. The nuclear spin-lattice relaxation rate is given by $T_1^{-1}\propto\gamma^2h_0^2J(\omega)$,[24] where J is the spectral density function of spin fluctuations, $\omega=2\pi\nu$ is the NMR frequency, and h_0 is the fluctuating component of the effective hyperfine field perpendicular to the applied field.

As we show in Fig. 3, the magnitude of $^{139}T_1^{-1}$ also depends strongly on the field orientation in the vicinity of T_f: $[^{139}T_1^{-1}(H\|c)]/[^{139}T_1^{-1}(H\perp c)]\cong 2.3\pm 0.3$ (see the ratio of C in Fig. 3), near 2, the value expected for XY-like spin fluctuations, where the fluctuations of the out-of-plane component are entirely frozen.[25] This striking XY-like behavior of spin fluctuations observed in this heavily doped system is

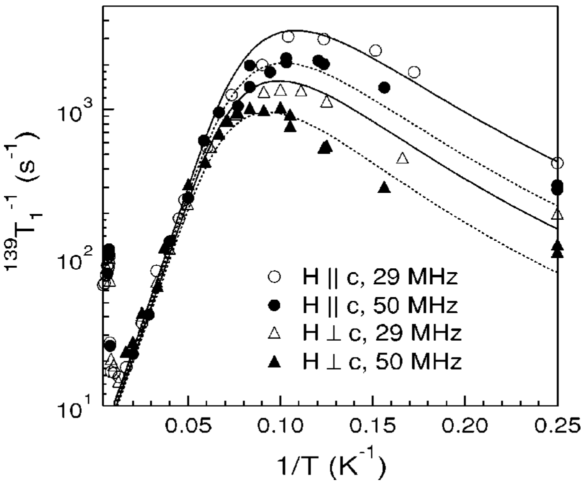

FIG. 3. $^{139}T_1^{-1}$ vs $1/T$. The curves are theoretical fits as described in the text using the fitting parameters: $E_0/k_B=82$ K, $\Delta=25$ K for both orientations and frequencies; for $H \| c{:}\,\tau_\infty=1.4\times10^{-13}$ s and $C=1.67\times10^{12}$ s^{-2}, and for $H\perp c{:}\,\tau_\infty=3.1\times10^{-13}$ s and $C=0.73\times10^{12}$ s^{-2}.

reminiscent of the crossover from Heisenberg to XY-like observed at temperatures just above the onset of long-range antiferromagnetic order in $Sr_2CuO_2Cl_2$.[25]

The frequency and temperature dependencies of $^{139}T_1^{-1}$ are well explained by the well-known BPP mechanism[21] that describes the effects of continuous slowing on the spin-lattice relaxation, although the anisotropic fluctuations and asymmetric peak evident in Fig. 3 are beyond the standard BPP picture. In particular, the stretched exponential recovery of the magnetization and the asymmetric peak implies a distribution of characteristic correlation times (τ_c) of the fluctuations.[26] We take $\tau_c(E_a,T)=\tau_\infty \exp(E_a/k_BT)$,[21] however, we must include a distribution of activation energies E_a (a Gaussian works well): $Z(E_a)=(\sqrt{2\pi}\Delta)^{-1}\exp[-(E_a-E_0)^2/2(k_B\Delta)^2]$. For two-dimensional diffusive fluctuations (in which c-axis fluctuations are frozen), we can write:[27] $J(\omega)=\tau_c \ln[(\tau_c^{-2}+\omega^2)/\omega^2]$. However, the much more general Lorentzian spectral density (applicable to fluctuations of all wavelengths) provides equally good fits with small changes in parameter values (E_0 and Δ differ by less than 20%). The measured relaxation rate will be an average over the distribution $Z(E_a)$:

$$T_1^{-1}(T)=C\int_0^\infty \tau_c \ln\left(\frac{\tau_c^{-2}+\omega^2}{\omega^2}\right) Z(E_a)dE_a\,, \qquad (1)$$

where the coefficient C is proportional to h_0^2. The fits shown in Fig. 3 demonstrate that the BPP picture (with a distribution of E_a) accurately describes $^{139}T_1^{-1}$at low T, accounting well for the frequency dependence evident at temperatures below the peak. This provides direct evidence for the *intrinsic role of disorder in the continuous slowing of the spin fluctuations.* Surprisingly, we find the ratio $[\tau_\infty^{-1}(H\|c)]/[\tau_\infty^{-1}(H\perp c)]\cong 2.2$ is essentially equal to the ratio of $^{139}T_1^{-1}$ (and the ratio of C). This is apparently related to the intrinsic anisotropy of two-dimensional spin system,[25] although it is not understood theoretically at present. (We note that studies of the stripe-ordered state of $La_{5/3}Sr_{1/3}NiO_4$ revealed no dependence of the static ordered magnetic moment on the orientation and magnitude of the applied magnetic field.[28]) The value of τ_∞ cannot be extracted from these fits with high precision (0.03psec$<\tau_\infty<$0.3 psec), however, the uncertainty in E_0 is much smaller ($82<E_0/k_B<96$ K). These slow fluctuations are in qualitative agreement with the slowing of fluctuations observed in ESR measurements.[11]

The strong similarity of the spin-freezing observed in the present metallic sample to that seen in lightly doped lanthanum cuprate is surprising given the broad range of doping involved and the strong consequent variation in magnetic properties. Scenarios have been proposed attributing spin freezing and the associated recovery of the sublattice magnetization observed in lightly hole-doped La214 to freezing of domain motion[14,29] or to the effective disappearance of domain boundaries as the constituent holes become pinned to the lattice at low T.[13] These do not appear applicable here: (i) Our heavily doped sample is a fair conductor whose resistivity ρ decreases with decreasing T to fairly low T with only a weak increase and a broad maximum below T_{LT}.[30] The magnitude of ρ itself is of the order $10^{-3}\,\Omega$ cm, one or two orders of magnitude smaller than in lightly doped La214. (ii) Neutron scattering shows the domain boundaries remain in the spin freezing regime.[5]

Two classes of mechanisms that could explain the spin freezing data in the present heavily doped sample can be considered. The first is related to scenarios previously discussed in the context of lightly doped lanthanum cuprate;[31–33] the low-temperature freezing could reflect the behavior of an ordered antiferromagnet spatially interrupted by an array of domain walls. The second involves the dynamics of charged domain walls.[34–36] This motion will alter the local magnetization in the spin ordered domains; the spin freezing would result from the gradual suppression of the excitations of this coupled system with decreasing temperature. The doping (and hence stripe density) independence of the freezing suggests that charge stripe dynamics are not responsible.[20] The distribution of activation energies we observe indicates that stripe defects and disorder are important.

We consider the first of these possibilities in the present more heavily doped sample: the spin freezing would reflect the slowing of fluctuations that would result as spin domains separated by charged domain walls become coupled allowing the correlation length to grow. At high T the coupling J' between individual spins separated by domain walls is likely weak compared to the exchange coupling constant J within a domain. However, the occurrence of long-range order at low T with correlation lengths long compared to the stripe spacing[5] indicates significant effective coupling between neighboring AF domains. The strength of the coupling between adjacent domains is proportional to $J'\xi^z$ where the spin correlation length ξ is a function of J and the exponent z is close to unity depending upon the dimensionality of domains. The very slow characteristic timescale ($\sim 10^{-13}$ s) and the XY-like character of the spin fluctuations we observe are consistent with a very large ξ above the apparent spin ordering temperature (≈ 20 K). At some low T, $J'\xi^z$ would become large enough ($\sim k_BT$) to couple neighboring domains; the characteristic fluctuation rate τ_c^{-1} will slow as the size of the correlated regions grow.

We now turn to the behavior of $^{63}T_1^{-1}$ which reflects the AF spin fluctuations and correlations. As shown in Fig. 2, $(^{63}T_1T)^{-1}$ exhibits Curie-Weiss behavior at high temperature above the opening of the spin pseudogap. The opening of the spin pseudogap is evident as a reduction of $(^{63}T_1T)^{-1}$ compared to the Curie-Weiss behavior resulting in a broad peak in $(^{63}T_1T)^{-1}$. The difference in the temperature dependencies of $(^{63}T_1T)^{-1}$ and $^{63}T_{2G}^{-1}$ below the peak position is indicative of the opening of a dynamic spin gap at $q=q_{AF}$.[1,37] Figure 2 shows $^{63}T_1^{-1}$ in lanthanum cuprate both with and without the Eu co-doping; the behavior is essentially identical down to ≈ 50 K), while below this $La_{1.8-x}Eu_{0.2}Sr_xCuO_4$ exhibits a substantially enhanced spin gap. It has been argued that a spin gap arises naturally in undoped spin ladders;[38,39] the enhanced spin gap observed in the LTT phase may arise from the improved confinement of the undoped domains into ladderlike structures by the static charge stripes at commensurate doping. In the spin freezing region below ≈ 20 K, $^{63}T_1^{-1}$ approaches a constant value in contrast to the rapid decrease in the superconducting $La_{2-x}Sr_xCuO_4$ (Ref. 2) (Fig. 2, inset); consistent with the absence of a superconducting transition in this spin freezing region.

We have presented a ^{139}La and ^{63}Cu NMR study of the spin dynamics in 1/8 doped, stripe-ordered $La_{1.67}Eu_{0.2}Sr_{0.13}CuO_4$. We show that the strong peak in $^{139}T_1^{-1}$ occurring below the AF ordering temperature is due to the well-known BPP mechanism.[21] The continuous slowing of spin fluctuations is characterized by a distribution of activation energies indicating the role of dynamical disorder in the previously noted quasistatic behavior,[8] in addition to static disorder.[10] We find the opening of the spin pseudogap is more pronounced in the presence of the static charge stripes at commensurate doping in the LTT phase. This suggests that the spin gap may be associated with the confinement of the spin regions separated by hole-rich domain walls.

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