Low Frequency Spin Dynamics in Undoped and Sr-Doped La_2CuO_4

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We report ^{63}Cu NQR and NMR studies of low frequency spin dynamics in the paramagnetic state of $La_{2-x}Sr_xCuO_4$ for $0 \le x \le 0.15$ in the temperature range up to 900 K. For $x=0$, the results were in good agreement with the theoretical predictions for an $S=\frac{1}{2}$ two-dimensional quantum Heisenberg antiferromagnet. For Sr-doped samples, we found that d spins exhibit, above 300 K, the characteristic behavior expected for a local moment system even for the highest-T_c phase $La_{1.85}Sr_{0.15}CuO_4$, and cross over to an itinerant regime before superconductivity sets in.

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It is well known that the parent materials of cupric high-temperature superconductors are insulating, quasi-two-dimensional antiferromagnets [1]; nevertheless band calculations predict they are metals [2]. This unambiguously demonstrates that there exist very strong carrier-carrier correlation effects in the parent materials when the nominal valence of copper ions is close to +2 as pointed out by Anderson [3]. When holes are doped into the CuO_2 sheets, the Néel temperature T_N decreases rapidly, followed by a crossover to a superconducting phase through a so-called spin-glass phase [4]. A number of anomalous experimental results have been reported for various physical properties in the normal state above T_c of the superconducting materials [4], suggesting the persistence of some sort of correlation effect.

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) have played a key role in elucidating the characteristics of the anomalous normal state of high-T_c superconductors [5]. Because of the experimental difficulties in observing the ^{63}Cu resonance signal in the paramagnetic state, however, very little has been known concerning the low frequency spin dynamics in the paramagnetic state of the undoped parent materials [6] and the spin-glass phase [7]. In this Letter, we report the first ^{63}Cu NQR study of the paramagnetic state of the antiferromagnetic parent material La_2CuO_4, and compare the results with the theoretical predictions by Chakravarty and Orbach based on the dynamical scaling theory for the two-dimensional quantum Heisenberg antiferromagnet (2D-QHAF) [8]. Because of its simplest layered structure, which includes only one CuO_2 sheet in the unit cell [4], La_2CuO_4 is an ideal system to perform such a study. We also report the influence of the hole doping for spin dynamics in the Sr-substituted isomorphs $La_{2-x}Sr_xCuO_4$ by varying the Sr concentration between the insulating phase and the metallic (and superconducting) phase. Surprisingly, very little influence of doping was observed for the ^{63}Cu nuclear spin-lattice relaxation rate $^{63}1/T_1$ at elevated temperatures.

All the powder ceramic samples studied in this work were prepared by the standard solid-state reaction technique [9]. Except for undoped La_2CuO_4, powders were annealed in oxygen gas atmosphere. For La_2CuO_4, the existence of a tiny amount of excess oxygen is known to cause a dramatic change in the electronic properties [10], which was actually observed in our NQR experiments. We therefore annealed powders in flowing nitrogen gas at 900 °C for 24 h to obtain stoichiometric $La_2CuO_{4.00}$. The absence of the excess oxygen is evidenced by a high Néel temperature $T_N=308\pm5$ K, which was determined by observing the splitting of the ^{139}La NQR line for the $\pm\frac{7}{2}$ to $\pm\frac{5}{2}$ transition. A standard homemade pulsed NMR spectrometer was utilized to carry out NQR and NMR experiments. Measurements at elevated temperatures were carried out in air. Weak signals were averaged up to 1×10^6 echoes when it was necessary.

First, we briefly discuss the results and the implications of NQR line-shape measurements. Shown in the inset of Fig. 1 is the ^{63,65}Cu NQR spectrum observed at 600 K

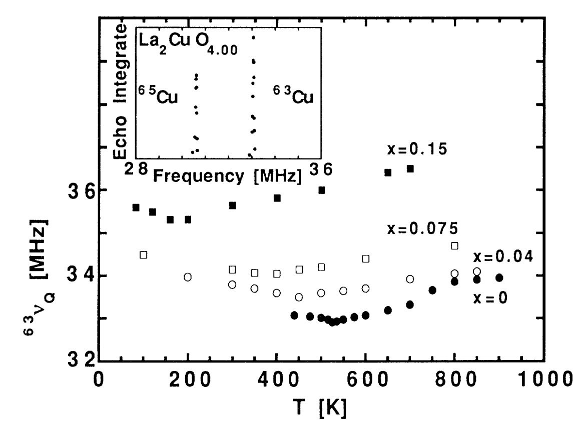

FIG. 1. Temperature and doping dependences of the ^{63}Cu NQR frequency, $^{63}\nu_Q$. Inset: NQR spectrum observed at 600 K for the clean sample of $La_2CuO_{4.00}$.

for $La_2CuO_{4.00}$. The observed linewidth, 55 ± 5 kHz, is 20 times narrower than that for Sr-doped samples [5]. This indicates that the Sr doping causes a substantial disorder in the CuO_2 sheet. The temperature and Sr concentration dependences of the ^{63}Cu NQR frequency $^{63}\nu_Q$ are shown in the main panel of Fig. 1. Throughout this work, the experimental errors of the data shown in the figures are about the size of the symbols. The sign of the temperature coefficient $d\,^{63}\nu_Q/dT$ changes from negative to positive at 180 ± 10, 380 ± 10, 450 ± 10, and 525 ± 2 K for $x=0.15$, 0.075, 0.04, and 0, respectively. These temperatures coincide with those of the orthorhombic-to-tetragonal structural phase transition, $T_{O\text{-}T}$ [4]. For $La_2CuO_{4.00}$, $^{63}\nu_Q$ exhibits a discontinuous increase when the sample was warmed up above 700 K in air. The thermogravimetric analysis showed that this is due to the absorption of excess oxygen $\delta = 0.0035 \pm 0.0005$, i.e., hole doping. We stress here that all the experimental results obtained below 700 K for $La_2CuO_{4.00}$ were completely reproducible as long as the sample was not warmed up above 700 K in air. The discontinuous increase of $^{63}\nu_Q$ for $La_2CuO_{4.00+\delta}$ compared with $La_2CuO_{4.00}$ is consistent with a systematic increase of $^{63}\nu_Q$ with Sr^{2+} doping for La^{3+}. After the sample was cooled down to 300 K from 900 K in air, $T_{O\text{-}T}$ and T_N for $La_2CuO_{4.00+\delta}$ were reduced from 525 ± 2 to 515 ± 2 K and from 308 ± 5 to 260 ± 5 K, respectively. Moreover, $^{63}1/T_1$ for $La_2CuO_{4.00+\delta}$ was enhanced compared with that for the clean sample of $La_2CuO_{4.00}$ (see the inset of Fig. 2), and did not follow the prediction of the dynamical scaling theory.

Presented in Fig. 2 is the temperature dependence of $^{63}1/T_1$ measured for insulating La_2CuO_4 as well as for $La_{2-x}Sr_xCuO_4$ [$x=0.04$ (nonsuperconducting spin-glass phase), $x=0.075$ ($T_c = 23$ K), and $x=0.15$ ($T_c = 38$ K, the maximum T_c phase)] by the NQR technique without applying an external magnetic field. As discussed above, the results obtained above 700 K for La_2CuO_4 should be regarded as the data for $La_2CuO_{4.00+\delta}$ ($\delta = 0.0035 \pm 0.0005$, $T_N = 260$ K). We note also that the results below 300 K for $x=0.075$ and 0.15 are in good agreement with earlier work [5,7]. Let us recall that $^{63}1/T_1$ reflects the weighted $\mathbf{q}$ average of $\chi''(\mathbf{q},\omega_0)$, the imaginary part of the transverse component of the dynamical electron spin susceptibility at the resonance frequency ω_0 [11], i.e.,

$$\frac{1}{^{63}T_1} = \frac{2k_BT}{g^2\mu_B^2\hbar^2}\sum_q A_{\mathbf{q}}^2 \frac{\chi''(\mathbf{q},\omega_0)}{\omega_0}, \tag{1}$$

where $A_{\mathbf{q}}$ is the $\mathbf{q}$-dependent hyperfine coupling constant at a site i defined by $A_{\mathbf{q}} = \sum_j A_{ij}\exp[i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)]$, A_{ij} is the interaction between the ith nuclear spin and the jth electronic spin, g represents the g factor, and $\mathbf{r}$ and $\mathbf{q}$ are coordinate and wave vectors, respectively. The most striking feature in Fig. 2 is that regardless of the doping level $^{63}1/T_1$ approaches nearly the same temperature-independent value 2700 ± 150 sec^{-1} at high temperatures. In other words, *at high temperatures the fundamental character of the Cu d spins in the metallic samples seems to be essentially the same as that in the insulating phase.* This result seems to rule out the theories which predict a concentration dependence for $^{63}1/T_1$ at high temperatures. By comparing the results for all samples, it is obvious that *the scattering with doped holes instead of exchange interaction becomes increasingly dominant in the spin fluctuation properties for the heavier doped samples especially at lower temperatures.*

With reducing temperature, the undoped $La_2CuO_{4.00}$ and the spin-glass phase $La_{1.96}Sr_{0.04}CuO_4$ exhibit a monotonic increase of $^{63}1/T_1$ due to the critical slowing down. Below 300 K, the spin echo decay time T_2 becomes gradually shorter for $La_{1.96}Sr_{0.04}CuO_4$. The extremely short T_2 (<5 μsec) has not allowed us to observe the signal below 100 K, which is consistent with an earlier report [7]. For both $La_2CuO_{4.00}$ and $La_{1.96}Sr_{0.04}CuO_4$, we found that there exists a small field dependence for $^{63}1/T_1$ by measuring it between 300 and 500 K for oriented ceramic powders using an NMR technique under the external magnetic field of 9.4 T applied parallel to the oriented c axis. That is, the transverse component of the critical fluctuations in the CuO_2 sheet is weakly suppressed ($\approx 10\%$) by the field applied perpendicular to the CuO_2 sheet. In the same temperature range, no field dependence ($<3\%$) of $^{63}1/T_1$ was observed for the other two superconducting samples.

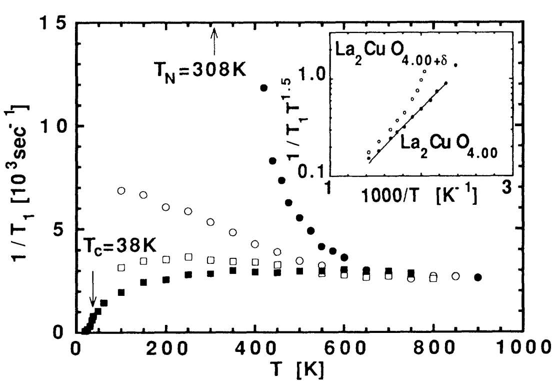

FIG. 2. Temperature dependence of $^{63}1/T_1$ measured by NQR for $La_{2-x}Sr_xCuO_4$ (●, $x=0$; ○, $x=0.04$; □, $x=0.075$; ■, $x=0.15$). The data below 100 K for $x=0.15$ are from Yoshimura *et al.* in Ref. [5]. Inset: The semilogorithmic plot of $^{63}1/T_1T^{3/2}$ (in units of sec^{-1}K$^{-1.5}$) vs $1000/T$ for the clean sample of $La_2CuO_{4.00}$ and for $La_2CuO_{4.00+\delta}$. The solid curve is the best fit by Eq. (2).

According to the theoretical calculations by Chakravarty and Orbach [8] based on the dynamical scaling hypothesis for an $S=\frac{1}{2}$ 2D-QHAF [12], $^{63}1/T_1$ in $La_2CuO_{4.00}$ is expected to satisfy the following relation in the critical region:

$$\frac{1}{^{63}T_1}=\frac{0.35}{Z_c}\frac{A_Q^2}{J\hbar}\frac{\xi}{a}\frac{(T/2\pi\rho_s)^{3/2}}{(1+T/2\pi\rho_s)^2}, \quad (2a)$$

$$\xi=\frac{0.27\hbar c}{2\pi\rho_s}\frac{\exp(2\pi\rho_s/T)}{1+T/2\pi\rho_s}, \quad (2b)$$

where J is the nearest-neighbor exchange interaction, a is the lattice constant, $\mathbf{Q}=(\pi/a,\pi/a)$, ξ is the antiferromagnetic correlation length, Z_c is a constant ($=1.18$), $2\pi\rho_s$ (stiffness constant) is $1.13J/k_B$, and c is the spin wave velocity ($=\sqrt{2}JaZ_c/\hbar$). When T is sufficiently smaller than $2\pi\rho_s$, Eqs. (2) predict that $\ln(^{63}1/T_1T^{3/2})$ is a linear function of $2\pi\rho_s/T$. Shown in the inset of Fig. 2 is the semilogarithmic is plot of $^{63}1/T_1T^{3/2}$ vs $1000/T$. Evidently Eqs. (2) properly describe the observed temperature dependence in a wide temperature range for the clean sample of $La_2CuO_{4.00}$. By choosing $2\pi\rho_s$ (hence J) and A_Q as two independent parameters, the data were fitted by Eqs. (2). We obtained $J=0.138\pm0.012$ eV ($J/k_B=1590\pm140$ K) and $A_Q/g\,^{63}\gamma_n\hbar=-139\pm10$ kOe/μ_B, where $A_Q=A_x-4B$, A_x and B are the x components of the on-site and the isotropic transferred hyperfine coupling constants, respectively [13], and $^{63}\gamma_n$ the nuclear gyromagnetic ratio of ^{63}Cu. It is worth noting that the fitted value of J decreases (increases) about 17% when the critical exponent $\frac{3}{2}$ in the numerator of Eq. (2a) is changed to 2 (1). The value of $J=0.138$ eV is in excellent agreement with the results obtained by Hayden *et al.* based on neutron scattering experiments, $J=0.132$ eV [14]. The value of the other fitted parameter A_Q agrees very well with the result estimated for $YBa_2Cu_3O_x$, $A_Q/g\,^{63}\gamma_n\hbar=-129$ kOe/μ_B [15]. We also found that the observed anisotropy of $^{63}1/T_1$ for $La_2CuO_{4.00}$ at 475 K, $^{63}R\equiv(^{63}1/T_1)_a/(^{63}1/T_1)_c=3.9\pm0.3$ where the subscripts a and c stand for the quantization axis of nuclear spins, is the same as $^{63}R=3.73$ observed for $YBa_2Cu_3O_7$ [16] within experimental errors. These results indicate that the hyperfine coupling constant tensor of $La_{2-x}Sr_xCuO_4$ is essentially the same as in $YBa_2Cu_3O_x$. We therefore take $A_x=38$ kOe/μ_B, $B=42$ kOe/μ_B, and $A_z=-167$ kOe/μ_B [15] in what follows. Combined with the zero field ^{63}Cu NMR frequency for the $\frac{1}{2}$ to $-\frac{1}{2}$ transition at helium temperature $(\mu_{\rm eff}/\mu_B)|A_Q|/g\hbar=92.89$ MHz observed by Tsuda *et al.* [17], we estimate the effective moment $\mu_{\rm eff}$ for the ground state of the $S=\frac{1}{2}$ 2D-QHAF as $(0.64\pm0.05)\mu_B$, where μ_B is the Bohr magneton. Again this is in excellent agreement with the theoretical predictions [18].

The homogeneous NQR linewidth measured by the Gaussian component of the spin echo decay rate, $^{63}1/T_{2G}$, provides another test for the scaling theory of 2D-QHAF. This is because $^{63}1/T_{2G}$ is dominated by the indirect nuclear spin-spin coupling $(a_{0j})^z$ in cuprates and $(a_{0j})^z$ is enhanced by the real part of the static susceptibility $\chi'(\mathbf{q})$ peaked at $\mathbf{q}=\mathbf{Q}$ as shown by Pennington and Slichter [19]. In the present case, one can show that $\chi'(\mathbf{q})$ is given by $\chi'(\mathbf{q})=2S(\mathbf{q})/k_BT$ in the scaling limit, where $S(\mathbf{q})$ is the static spin-spin correlation function defined in Ref. [12]. Since J, hence $\xi\sim\exp(2\pi\rho_s/t)$ which determines $\chi'(\mathbf{q})$, is already determined above, there is no adjustable parameter for $\chi'(\mathbf{q})$. We estimate $^{63}1/T_{2G}=(8.2\pm1.7)\times10^4$ and $(4.8\pm0.95)\times10^4$ sec^{-1} at 500 and 600 K, respectively, in reasonable agreement with our experimental results, $(6.3\pm0.3)\times10^4$ and $(3.9\pm0.2)\times10^4$ sec^{-1}.

Next we turn to the high-temperature behavior of $^{63}1/T_1$, where $^{63}1/T_1$ is essentially temperature and concentration independent (2700 ± 150 sec^{-1}). Moriya [20] calculated $1/T_1$ at the site of a magnetic ion for the *exchange narrowed* regime based on a Gaussian autocorrelation function of a spin S_0:

$$\langle S_0^\alpha S_0^\alpha(t)\rangle=[S(S+1)/3]\exp(-\omega_e^2t^2/2), \quad (3a)$$

$$\omega_e^2=n(J^2/\hbar^2)S(S+1)/3, \quad (3b)$$

where $\alpha=x$, y, or z, n is the number of nearest-neighbor spins, and ω_e is the correlation frequency. It is easy to extend Moriya's calculations to the present case of the square lattice under the presence of the isotropic transferred hyperfine interaction B by explicitly calculating the nearest-neighbor spin correlation function $\langle S_0^\alpha S_k^\alpha(t)\rangle$. The result of the high-temperature limit of $^{63}1/T_1$ is, again within the Gaussian approximation,

$$\frac{1}{^{63}T_{1\infty}}=\sqrt{2\pi}(A_x^2+4B^2)\frac{S(S+1)}{3\hbar^2\omega_e'}, \quad (4)$$

where $\omega_e'=\omega_e[1-2A_xB/(A_x^2+4B^2)]^{1/2}$. Taking $S=\frac{1}{2}$, we estimate $^{63}1/T_{1\infty}=4500\pm1300$ sec^{-1}. This is 2 times faster than our experimental results. With reducing the temperature, the growth of the short-range order is expected to *reduce* $^{63}1/T_1$ gradually until the critical slowing down sets in [20]. According to the detailed theoretical calculations based on the high-temperature expansion by Singh and Gelfand [21] and the finite cluster method by Sokol, Bacci, and Gagliano [22], $^{63}1/T_1$ does not show a strong temperature dependence around $T\approx0.5J/k_B$ with a value of $\approx0.45(^{63}1/T_{1\infty})$. Combined with our estimate of $^{63}1/T_{1\infty}$, we expect $^{63}1/T_1=2000\pm600$ sec^{-1}, in reasonable agreement with experimental results. This leads us to conclude that *the observed $^{63}1/T_1\approx2700$ sec^{-1} is dominated by the short-range order, and the doped holes do not change the short-range order significantly down to $T\approx J/2k_B$.* Since $1/T_1$ is inversely proportional to J as shown by Eq. (4), we conclude also that *the nearest-neighbor exchange interaction $J\approx0.13$ eV is almost independent of doping.* For $La_{1.925}Sr_{0.075}CuO_4$ ($T_c=23$ K), $^{63}1/T_1$ weakly increases down to a temperature we call T^* (≈300 K). Here we identify T^* as the temperature where $^{63}1/T_1$ deviates from the behavior at higher temperature. We found quite similar behavior for $La_{1.92}Ba_{0.08}CuO_4$. The observed increase of $^{63}1/T_1$ down to T^* for 7.5%–8% doping indicates that the doped 2D-QHAF is trying to approach an ordered ground state down to T^* even in the material which can become superconducting. In the case of $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K), $^{63}1/T_1$ is temperature independent within $\pm 3\%$ down to $T^* \approx 300$ K, i.e., there is no critical slowing down. This indicates that already above T^* the d spins are aware that the ground state is no longer an antiferromagnetic insulator. Below T^*, $^{63}1/T_1$ decreases monotonically down to T_c. Above 100 K, the anisotropy of $^{63}1/T_1$ for $La_{1.85}Sr_{0.15}CuO_4$ is $^{63}R = 2.6 \pm 0.2$ as reported by Imai *et al.* [7], approximately 30% smaller than the values observed for $La_2CuO_{4.00}$ (3.9 ± 0.3 at 475 K), $La_{1.96}Sr_{0.04}CuO_4$ (3.5 ± 0.3 at 300 K), and $YBa_2Cu_3O_7$ (3.73 above T_c) [16]. Since the anisotropy is very sensitive to the piling up of $\chi''(\mathbf{q},\omega_0)$ around $\mathbf{q} = (\pi/a, \pi/a)$ [15,23], this indicates that $\chi''(\mathbf{q},\omega_0)$ has a substantial spectral weight away from $\mathbf{q} = (\pi/a, \pi/a)$. Just below T_c, $^{63}1/T_1$ exhibits a dramatic power-law-like decrease [5]. This undoubtedly demonstrates that d spins are itinerant and involved in the Cooper pairing at T_c. In other words, *the d spins gradually undergo a crossover from a paramagnetic spin fluctuation regime of essentially localized moments to a more itinerant regime around T^* before superconductivity sets in.* A similar situation is frequently encountered for heavy fermion materials [24]. Finally it is very interesting to notice that there is a qualitative difference in the behavior of $^{63}1/T_1$ between $La_{1.85}Sr_{0.15}CuO_4$, which includes only one CuO_2 sheet in the unit cell, and $YBa_2Cu_3O_7$, which has double CuO_2 sheets in the unit cell. In the latter case, $^{63}1/T_1$ increases monotonically above $T^* \approx 200$ K as $^{63}1/T_1 \approx a + bT$, where a and b are constants [25].

In conclusion, we carried out ^{63}Cu NQR and NMR studies of the undoped and Sr-doped La_2CuO_4. For the undoped $La_2CuO_{4.00}$, we demonstrated that both the dynamic and static magnetic properties in the paramagnetic state as well as the staggered moment in the ground state agree with the predictions of the existing theories for the $S = \frac{1}{2}$ two-dimensional quantum Heisenberg antiferromagnet. For hole-doped systems, we found that $^{63}1/T_1$ shows very little doping dependence at high temperatures ($\approx J/2k_B$), suggesting that the local moment character of Cu d spins in the insulating phase are preserved even in the metallic phase. We also showed that d spins undergo a crossover to a more itinerant regime below $T^* \approx 300$ K before superconductivity sets in.

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