Spin-Spin Correlation in the Quantum Critical Regime of La$_2$CuO$_4$

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We report measurements of the $^{63}$Cu nuclear spin echo decay rate $1/T_{2G}$ in the paramagnetic state of a quasi-two-dimensional antiferromagnet La$_2$CuO$_4$ up to 900 K, and from it deduce the temperature dependence of the spin-spin correlation length $\xi$. $\xi$ shows a crossover from $\xi \sim \exp(J/k_BT)$ in the renormalized classical regime ($T \lesssim 600$ K) to $\xi \sim J/k_BT$ in the quantum critical regime ($T \gtrsim 600$ K), where $J$ is the exchange interaction. Our finding that the ratio $T_{1T}/T_{2G}$ is temperature independent, where $T_{1T}$ is the $^{63}$Cu nuclear spin-lattice relaxation time, gives clear evidence for quantum critical scaling.

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The discovery of high-$T_c$ superconductivity in doped La$_2$CuO$_4$ promoted strong interest in the physical properties of the undoped antiferromagnetic parent material because of its low dimensionality and strong quantum phenomena [1]. It is firmly established that the magnetism of La$_2$CuO$_4$ can be described very well based on the two-dimensional Heisenberg model with a nearest neighbor exchange interaction $J$ ($\approx$ 1500 K) [2],

$$ H = \sum_{i\neq j} J S_i S_j, $$

where $S_i$ is a copper d spin ($S = \frac{1}{2}$) at a lattice site $i$. A weak intralayer coupling induces a three-dimensional antiferromagnetic ordering at $T_N \approx 300$ K. Neutron scattering experiments by the Brookhaven Collaboration carried out up to 540 K demonstrated that the copper spin-spin antiferromagnetic correlation length $\xi$ shows a very strong temperature dependence even far above $T_N$ [3]. Chakravarty, Halperin, and Nelson [4] showed theoretically that there are two regimes in the paramagnetic state of La$_2$CuO$_4$. One is the renormalized classical regime, $T_N < T \lesssim 2 \rho_s$ ($\rho_s \approx 0.18 J \approx 300$ K is the spin stiffness constant), where $\xi$ is shown to satisfy an exponential temperature dependence [4,5],

$$ \frac{\xi}{a} = \frac{0.498}{1 + 0.5(2\rho_s)/T} \exp\left(\frac{2\pi \rho_s}{\xi} \right). $$

$a$ is the in-plane lattice constant (3.8 Å), $k_B$ is the Boltzmann constant. The other is the quantum critical regime ($2\rho_s \lesssim T$), where $\xi$ satisfies

$$ \frac{\xi}{a} \sim c_0 \hbar c / k_B T. $$

$c_0$ is a constant of order of unity, $\hbar c = \sqrt{2}JaZ_c$ ($Z_c = 1.158$) is the spin wave velocity.

Very recently Imai et al. [6] reported that the $^{63}$Cu nuclear spin-lattice relaxation rate $1/T_{1T}$ in La$_2$CuO$_4$ satisfies a simple relation $1/T_{1T} \sim T^{-1.2} \xi^{-1.2} \exp(2\pi \rho_s/k_BT)$ in the renormalized classical regime as predicted by Chakravarty and Orbach [7]. Their observation, as well as neutron scattering experiments by Yamada et al. [8], strongly supports the dynamical scaling theory [4] employed by Chakravarty, Halperin, and Nelson to relate the dynamical structure factor $S(q, \omega)$ with the equal time correlation function $S(q)$, where $q$ and $\omega$ are wave vector and frequency, respectively. The $^{35}$Cl NMR experiments for a similar material Sr$_2$CuO$_2$Cl$_2$ by Borsa et al. [9] also showed the validity of the dynamical scaling at low temperatures [9]. However, Imai et al. also found that $1/T_{1T}$ levels off to $\approx 2.8 \times 10^3$ above 650 K, which clearly indicates the breakdown of the renormalized classical behavior. Moreover they found that even the Sr-doped high-temperature superconducting phase La$_{0.85}$Sr$_{0.15}$CuO$_4$ exhibits essentially the same behavior at high temperatures. Chubukov and Sachdev [10] pointed out that these results can be accounted for by quantum critical scaling [4,10] which relates $S(q, \omega)$ and $S(q)$ differently from the case of dynamical scaling. More recently Sokol and Pines [11] showed that quantum critical scaling can be verified if the ratio $[631/T_{2G}]^{631}/T_{1T}]$ is temperature independent, where $1/T_{2G}$ is the Gaussian component of the $^{63}$Cu nuclear spin echo decay rate, and used it as a base for their discussion of the unified picture of the phase diagram of La and Y cuprates.

Prior to the present work, there has been no experiment in the quantum critical regime of La$_2$CuO$_4$ other than our $1/T_{1T}$ measurements [6] because of technical difficulties at high temperatures. In the present paper, we report the temperature dependence of $1/T_{2G}$ between 450 and 900 K, i.e., in both the renormalized classical and quantum critical regimes. As explained below, $1/T_{2G}$ is known to give quantitative information regarding $\chi'(q)$, the real part of the wave vector $q$ dependent static spin susceptibility, and hence allows us to determine the correlation length $\xi$ [12]. Our results are the first measurements of the temperature dependence of $\xi$ in
the quantum critical regime of La$_2$CuO$_4$. We test Eq. (4) for $\xi$ in the quantum critical regime, and demonstrate that the linear temperature dependence of $1/\xi$ [4] with positive intercept [10], $1/\xi \sim T^{1\text{+const}}$, indeed holds. By comparing the results of $^{63}$T$_1$/T$_{2G}$ [~ $\sqrt{\sum q |\chi(q)|^2}$, see below] and $^{63}$T$_1$/T$_{2G}$ [~ $T \sum q |\chi^n(q,\omega_n)|^2$], we will also present an unambiguous experimental evidence that $^{63}$T$_1$/T$_{2G}$ is temperature independent, as predicted by Sokol and Pines [11], so that $\chi^n(q,\omega_n)$ and $\chi(q)$ exhibit quantum critical scaling [4,10].

The $^{63}$Cu NQR and NMR experiments were carried out utilizing the standard pulsed NMR spectrometer of our laboratory. In our previous study, a tiny amount of oxygen (6~0.0035 per cell unit) was absorbed by the polycrystalline sample warmed up in air, resulting in the motional narrowing effect [14] above 600 K possibly due to the fast motion of the excess oxygen atoms. This did not allow us to measure the temperature dependence of $^{63}$T$_1$/T$_{2G}$ [6]. To avoid oxygen absorption, our new sample ($T_N$ = 308 K) was sealed in a quartz vacuum tube whose diameter is 5 mm. The temperature dependence of the $^{63}$Cu NQR frequency did not reveal any anomaly around 750 K, indicating that no absorption of the oxygen into the sample took place in the process of our measurements in our present report. The refined data of $^{63}$T$_1$/T$_1$ measured by NQR showed perfect agreement with our published results [6]. Comparison of the $1/T_1$ measured for $^{63}$Cu and $^{65}$Cu isotopes indicated that the spin-lattice relaxation is completely dominated by magnetic relaxation processes in the entire temperature range.

The Gaussian component of the $^{63}$Cu nuclear spin echo decay rate $^{63}$T$_1$/T$_{2G}$ was obtained by fitting the time evolution of the integrated intensity of the spin echo $M(2t)$ as a function of the separation time $t$ between the exciting and the refocusing pulses to the following formula with two independent parameters $M_0$ and $T_{2G}$.

$$M(2t) = M_0 \exp \left( \frac{-2t}{T_{2G}} \right) \exp \left( -\frac{(2t)^2}{2(T_{2G})^2} \right).$$

The contribution of the spin-lattice relaxation processes to the spin echo decay, $^{63}$T$_1$/T$_{2G}$, was determined by use of the Redfield theory [14] as $^{63}$T$_1$/T$_{2G} = (\beta + R)(^{63}$T$_1$) [15]. The value of $\beta$ is 2 and 3 for NQR and NMR measurements, respectively, while $R$ is the anisotropy of $^{63}$T$_1$, $R = 3.6 \pm 0.2$. As shown in Fig. 1, we clearly observed a contribution of a Gaussian decay as reported previously for YBa$_2$Cu$_3$O$_7$ [16,17]. Our key result, the temperature dependence of $^{63}$T$_1$/T$_{2G}$ measured by NQR, is presented in Fig. 2. To facilitate comparisons, we converted our NQR data to the values expected for the NMR measurements of the $T_1$ to $T_{2G}$ transition by multiplying our raw data of $^{63}$T$_1$/T$_{2G}$ by a factor $1.07/\sqrt{2}$ [18].

As stressed by some of us before [17], $^{63}$T$_1$/T$_{2G}$ can be measured correctly only when the linewidth of the resonance line $\Delta f$ is sufficiently narrow compared with the strength of the rf pulses $H_1$. The NQR technique can be applied to La$_2$CuO$_4$ merely because $\Delta f$, which is primarily dominated by the mechanism of homogeneous broadening [14], is exceptionally narrow [6]. In fact the temperature-dependent NQR linewidth $\Delta f$ is an order of magnitude narrower at high temperatures ($\Delta f = 24 \pm 2$ kHz at 900 K) than that of high-temperature superconducting materials whose NQR linewidth is dominated by inhomogeneous broadening induced by disordering. Since $\Delta f$ is nearly proportional to $^{63}$T$_1$/T$_{2G}$ and diverges with lowering temperature, we checked at 300 K that the fitted value of $^{63}$T$_1$/T$_{2G}$ does not deviate even if we reduce $H_1$ by 50%.

If only the nuclear dipole-dipole interaction contributes to $^{63}$T$_1$/T$_{2G}$, the results should be temperature independent with a much slower rate, $\sim 1800$ sec$^{-1}$. Pennington et al. [16] concluded from their single crystal NMR experiments for YBa$_2$Cu$_3$O$_7$ that the c-axis component of the indirect nuclear spin-spin coupling [14] dominates $^{63}$T$_1$/T$_{2G}$ in high-$T_c$ cuprates. In such a case, Pennington and Slichter showed that $^{63}$T$_1$/T$_{2G}$ measured for the $T_1$ to

![FIG. 1](image1.png)

**FIG. 1.** The time evolution of the Gaussian component of the integrated intensity of $^{63}$Cu NQR spin echo, $M(2t)/M_0 \times \exp(-2t/T_{2G})$. The straight line is the best fit by Eq. (4).

![FIG. 2](image2.png)

**FIG. 2.** $^{63}$T$_1$/T$_{2G}$, $^{63}$T$_1$. Experimental errors are about the size of the symbols. $\bigcirc$: The ratio $^{63}$T$_1$/T$_{2G}$.
\( - \frac{1}{2} \) transition by NMR can be related to \( \chi'(q) \) by the following relation [12,19]:

\[
\left( \frac{1}{T_{2G}} \right)^2 = \frac{0.69}{2\hbar^2} \left[ \frac{1}{N} \sum_q f_\epsilon(q) \chi'(q)^2 \right] - \left( \frac{1}{N} \sum_q f_\epsilon(q) \chi'(q) \right)^2 .
\] (5)

The factor 0.69 originates from the natural abundance of \( ^{63}\text{Cu} \). \( f_\epsilon(q) = A_c + 2B_l \cos(q,a) + \cos(q,a) \) is the form factor originating from the hyperfine interaction between the nuclear spin and the surrounding electron spins [20]. A_c and B are the c-axis component of the nearest neighbor and the transferred hyperfine interaction, respectively. The physical origin of the relation between \( T_{2G} \) and \( \chi'(q) \) results from the following: The hyperfine field that originated from a nuclear spin polarizes surrounding electron spins through nonlocal electron spin susceptibility \( \chi'(r',\mathbf{r}) = (1/N) \sum_q \epsilon_{\mathbf{q}} \hat{q}^{(r',\mathbf{r})} \chi(q) \), and the polarized electron spins in turn interact with another nuclear spin. Since the range of \( \chi'(r',\mathbf{r}) \) is the correlation length \( \xi \), the temperature dependence of \( \xi \) can be determined by the measurement of \( T_{2G} \). Since the form factor \( f_\epsilon(q) \) is peaked at \( q = (\pi/a, \pi/a) \) in the present case [20], \( T_{2G} \) is dominated by the short wavelength component of \( \chi(q) \). The observed monotonic increase of \( T_{2G} \) in Fig. 2 therefore indicates that \( \chi'(q) \) around the staggered wave vector \( q = (\pi/a, \pi/a) \) increases monotonically with lowering temperature due to the growing antiferromagnetic correlation. It is worthwhile noting that the long wavelength susceptibility \( \chi'(\mathbf{q} = 0) \) decreases in the same temperature range [1,2].

If one has an explicit form for \( \chi'(q) \), Eq. (5) can be evaluated. If the functional form depends on parameters such as \( T \) and \( \xi \), one can deduce the temperature dependence of \( \xi \) from the data of \( T_{2G} \). Chakravarty and co-workers [4] showed that \( \chi'(q) \) can be expressed by a nearly Lorentzian formula in the renormalized classical regime (\( T \leq 600 \) K),

\[
\chi'(q) = \frac{g^2 \mu_B N_0 B_s \xi^2}{3k_B T(2\pi \rho_s/T + 1)^2} \left[ 1 + (2\pi/B_s) \ln \left( 1 + q^2 \xi^2 \right) \right]^{-1} .
\] (6)

where \( B_s = 10^{-2} \), \( N_0 = 0.31 \), \( g = 2 \), and \( \mu_B \) is the Bohr magneton. A subsequent Monte Carlo study by Makić and Jarrel [21] found Eq. (6) is valid even in higher temperatures with \( B_s = 55 \). More recently the numerical calculations by Glenister, Singh, and Sokol [22] based on the high-temperature expansion technique showed that, to a good approximation, a simple Lorentzian formula \( \chi'(q) \approx \xi^2/(1 + q^2 \xi^2) \) reproduces their results in the quantum critical regime (\( T \geq 600 \) K). Since the temperature-dependent coefficient \( 1/T(2\pi \rho_s/T + 1)^2 \) of Eq. (6) is nearly temperature independent (within \( \sim 17\% \)) between 600 and 900 K, we may use Eq. (6) in the entire temperature range of Fig. 2. We note that our definition of \( \xi \) is based on the width of static susceptibility \( \chi'(q) \). Our definition coincides with the renormalized classical regime with that of neutron scattering experiments, in which \( \xi \) is defined as the width of the equal time correlation function \( S(q) \), because \( \chi'(q) = S(q)/k_B T \) holds in the limit of dynamical scaling.

In the inset to Fig. 3, we show a fit of \( 631/T_{2G} \) by Eq. (6) using Eq. (2). We inserted the neutron value \( 2\pi \rho_s = 1.13J = 1730k_B T = 0.132 \) eV [23], and normalized the integral by picking \( B_s = 39 \) to fit the value of \( 631/T_{2G} \) below 600 K. The deviation from the renormalized classical behavior makes the fit increasingly poor in the quantum critical regime above 600 K. Plotted in the main panel of Fig. 3 is the temperature dependence of \( a/\xi \) determined by using Eqs. (5) and (6) for the value of \( B_s \) determined by Monte Carlo calculations \( B_s = 55 \) [21]. Essentially all that is assumed here is a Lorentzian-like \( q \) dependence. The results do not change appreciably even if we neglect the log term in Eq. (6) as shown in Fig. 3. A different choice for the value of \( B_s \) does not change the qualitative aspects of the temperature dependence of \( a/\xi \) in Fig. 3. Evidently, the results in the renormalized classical regime agree very well with neutron data by Keimer et al. [3]. Above 600 K, the observed temperature dependence of \( a/\xi \) can be approximated very well by \( a/\xi \approx \xi(T - T_0) \), where \( T_0 = 400 \) K and \( \xi \sim 2 \times 10^{-4} \). This \( T \)-linear behavior with positive intercept is consistent with the theoretical prediction based on the quantum critical scaling theory [4,10] and high-temperature expansion [22]. We also note that the first-principles calculations in Ref. [22] reproduce our data of \( 631/T_{2G} \) quantitatively without any adjustable parameters.

Another striking feature of our experimental results may be seen in Fig. 2, where we plotted the ratio of \( 631/T_{2G} \) and \( 631/T_{2G} \). We find that \( 631/T_{2G} \approx 4.2 \times 10^3 \) K is temperature independent to a high degree of

![FIG. 3. The temperature dependence of \( a/\xi \) determined by \( 631/T_{2G} \) using Eq. (6) for \( B_s = 55 \) and \( B_s = 0.23 \). (a) \( a/\xi \) when the log term of Eq. (6) is neglected (i.e., for \( B_s = 55 \) and \( B_s = 0 \)). (b) \( a/\xi \) determined by neutron scattering (after Ref. [3]). Solid lines are the best fits by \( a/\xi = \xi(T - T_0) \). Inset: \( 631/T_{2G} \) (sec\(^{-1}\) K\(^{-1}\)) as a function of 1000/T (K\(^{-1}\)). The dotted curve is a fit by Eq. (6) with exponentially temperature-dependent \( \xi \) described by Eq. (2).]
precision between 450 and 900 K. This indicates that there is a scaling relation between \(\chi'(q)\) and \(\chi''(q,\omega)\) as discussed below. The results, however, disagree with the prediction of the dynamical scaling theory, 

\[ \frac{61}{T_1 T} \sim T^{1.2} \xi \quad \text{and} \quad \frac{61}{T_{2G}} \sim \xi^2 \]  

[4,7], hence \(\frac{61}{T_1 T_{2G}} \sim T^{0.5}\). On the other hand, Sokol and Pines [11] predicted very recently that

\[ \frac{61}{T_1 T_{2G}} = \text{const} + O(\rho_s/T), \]

(7)

based on the quantum critical scaling theory [4,10]. Sokol and Pines also showed using the finite cluster method that the quantity \(\frac{61}{T_1 T_{2G}} \sim 4.3 \times 10^{-3}\) K is nearly temperature independent around \(T \sim 750\) K. This means that the correction term \(O(\rho_s/T)\) in Eq. (7) is actually very small, and the temperature independence of \(\frac{61}{T_1 T_{2G}}\) is a criterion for quantum critical scaling. We therefore conclude that the quantum critical scaling hole in the quantum critical regime \(T \approx 600\) K of \(La_2CuO_4\). The fact that \(\frac{61}{T_1 T_{2G}}\) is temperature independent down to 450 K suggests that the crossover from the renormalized classical regime \(\xi < 2\rho_s/T\) at \(T \ll 2\rho_s\), where the dynamical scaling hypothesis should hold, to the quantum critical regime \(\frac{61}{T_1 T_{2G}} \sim \text{const} \) and \(\xi \sim 1/T\) at \(T \approx 2\rho_s\) takes place smoothly in the interval of a broad temperature range.

In conclusion, we report the temperature dependence of the \(61\) nuclear spin echo decay rate \(\frac{61}{T_{2G}}\) in both the renormalized classical and quantum critical regimes of a quasi-two-dimensional antiferromagnet \(La_2CuO_4\). The temperature dependence of the antiferromagnetic correlation length \(\xi\) was determined from the data of \(\frac{61}{T_{2G}}\). The results in the renormalized classical regime agreed with neutron scattering data. The temperature dependence of \(\xi\) showed a crossover above 600 K from an exponential law to a quantum critical behavior, \(1/\xi \sim T + \text{const}\). Moreover, the ratio \(\frac{61}{T_1 T_{2G}}\) was found to be temperature independent. These results unambiguously establish that the high-temperature properties of \(La_2CuO_4\) can be explained by quantum critical scaling.

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[18] The time-dependent density matrix \(\rho_s(t)\) in the rotational frame for a spin echo of a two level nuclear spin system, formed by applying two rf pulses along the rotational \(x\) axis that flip nuclear spins by angles \(\theta\) and \(2\theta\), can be written as \(\rho_s(t) = I_x \sin^2 \theta \sin^2 \theta \cos^2 \alpha_f + \cos^2 \theta \). \(\alpha_f\) is the indirect nuclear spin-spin coupling constant. \(I_x\) is the nuclear spin operator. By taking the powder average over \(\theta\), we found theoretically that NQR measurements of \(\frac{61}{T_{2G}}\) for uniaxially aligned powders gives a 7% larger value than that for random powders, which we confirmed experimentally at 500 K. The additional factor \(1/\sqrt{2}\) also appears because the number of nuclear spins flipped is a half for NMR measurements, which was also confirmed experimentally at 500 K.

[19] For a transformation of the expression of \(\frac{61}{T_{2G}}\) derived primarily in the real space in Ref. [12] to that in q space, see D. Thelen and D. Pines (unpublished).