Dynamics in the $S = 1/2$ One-Dimensional Antiferromagnet Sr_2CuO_3 via ^{63}Cu NMR

M. Takigawa,[1] N. Motoyama,[2] H. Eisaki,[2] and S. Uchida[2]
[1]*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*
[2]*Department of Superconductivity, University of Tokyo, Tokyo 113, Japan*
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The ^{63}Cu nuclear spin-lattice relaxation rate ($1/T_1$) and the Gaussian spin-echo decay rate ($1/T_{2G}$) have been measured in the spin 1/2 one-dimensional antiferromagnet Sr_2CuO_3 ($J = 2200$ K) in the temperature range from 20 to 280 K. We observed the following temperature dependencies: $1/T_1 = \text{const}$ and $1/T_{2G} \propto 1/\sqrt{T}$, consistent with scaling theory. The value of $T_1\sqrt{T}/T_{2G}$ is also in good agreement with theoretical prediction. These results provide strong experimental support for the quantum critical behavior of the $S = 1/2$ 1D Heisenberg model at finite temperatures. [S0031-9007(96)00458-9]

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Recent progress in field theoretical methods and numerical simulations has significantly improved our understanding of low-dimensional quantum antiferromagnets. Many efforts have focused on the calculation of the dynamic spin susceptibility $\chi(q, \omega)$ in one-dimensional (1D) Heisenberg models [1–3]. Half-integer spin chains possess a subtle critical nature. Although the antiferromagnetic correlation length diverges at $T = 0$, substantial 1D quantum spin fluctuations suppress the long range order and spin correlation shows a power law decay [4,5]. Indeed the field theoretical result for $\chi(q, \omega)$ obtained by Schulz [3], which explains the recent neutron scattering data in $KCuF_3$ quite well [6], satisfies a scaling relation analogous to what has been proposed for the 2D antiferromagnets at the critical point where the long range order vanishes [7].

Nuclear magnetic resonance (NMR) experiments provide us with useful information on spin dynamics. The temperature (T) dependencies of both the spin-lattice relaxation rate ($1/T_1$), which probes the low frequency dynamic susceptibility, and the Gaussian spin-echo decay rate ($1/T_{2G}$), which is given by the static susceptibility, reflect the scaling behavior of the spin chains. Recently, Sachdev has shown that the scaling theory for half-integer spin chains leads to the following T dependencies: $1/T_1 = \text{const}$ and $1/T_{2G} \propto 1/\sqrt{T}$ [8]. Recent quantum Monte Carlo (QMC) calculations by Sandvik [9] support this result for an appropriate range of temperature and hyperfine parameters. Experimentally, nearly constant $1/T_1$ has been observed at low temperatures in some $S = 1/2$ antiferromagnetic chain compounds [10–12]. The analysis of these results, however, should be reexamined in the light of current theoretical understanding. Also, to our knowledge, no $1/T_{2G}$ data in spin chains have been reported.

Recent studies [13–15] have shown that Sr_2CuO_3 has excellent 1D character. The crystal structure [14] is similar to La_2CuO_4, but there is no oxygen between the two copper neighbor atoms along one direction in the CuO layers. (This direction is defined to be the c axis.) The remaining in-plane and apical oxygens form linear CuO_2 chains along the b axis. The a axis is taken to be the direction connecting copper and apical oxygen. The T dependence of the susceptibility shows good agreement with the exact calculation for the 1D $S = 1/2$ Heisenberg model [16] with the exchange energy $J = 2200 \pm 200$ K [15]. This is many orders of magnitude larger than the 3D ordering temperature $T_N = 5$ K, which has been determined from muon spin rotation and neutron experiments [13,17]. In this paper we report the results of $1/T_1$ and $1/T_{2G}$ for ^{63}Cu nuclei in the T range from 20 to 280 K, which show good quantitative agreement with the scaling theory and QMC calculations. Ishida *et al.* [18] have recently reported T-independent $1/T_1$ in the isostructural compound Ca_2CuO_3.

The NMR experiments were performed on a single crystal of Sr_2CuO_3 grown by the traveling-solvent-floating-zone method, followed by annealing in an Ar atmosphere to reduce the impurity Curie term in the susceptibility [15], which corresponds to a few hundred ppm of free $S = 1/2$ impurity spins. Sharp NMR spectra split by the quadrupole interaction were obtained at room temperature [19]. We measured $1/T_1$ for ^{63}Cu nuclei by the inversion recovery method on one of the quadrupole split lines at a magnetic field (H) of 8 T. The relaxation of the nuclear magnetization over nearly three decades could be fit assuming no distribution in $1/T_1$. From the ratio of $1/T_1$ for the two Cu isotopes, the relaxation process was confirmed to be magnetic over the whole temperature range. The spin-echo decay was measured for $H \parallel c$ on one of the quadrupole split ^{63}Cu lines, which was then fit by the form $M_0 \exp(-t/T_{2L} - t^2/2T_{2G}^2)$ with the value of $1/T_{2L}$ (contribution from the spin-lattice process) determined from the $1/T_1$ data [20]. Good fitting was obtained over more than two decades. The NMR lines were narrow enough above $T = 60$ K to ensure complete inversion by the π pulse at $H = 8$ T. (The FWHM was less than 70 kHz.) At lower temperatures, the lines became broader and the spin-echo decay was measured at 2.2 T with reduced line width. We confirmed that the results do not depend on the magnetic field.

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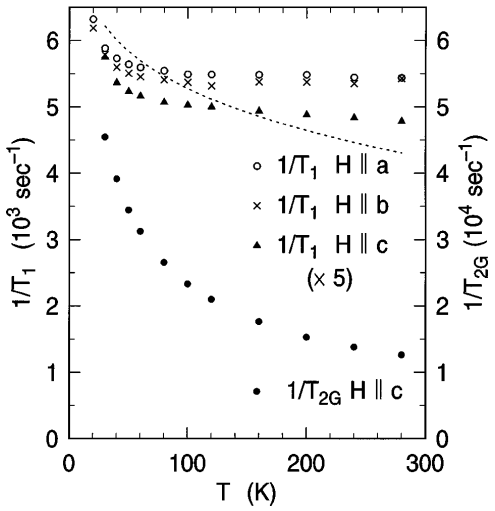

FIG. 1. The T dependencies of $1/T_1$ for three field directions (scale on the left axis) and $1/T_{2G}$ for $H \parallel c$ (scale on the right axis). The $1/T_1$ data for $H \parallel c$ are multiplied by a factor of 5. The dotted line indicates the $\ln^{1/2}(J/T)$ dependence with arbitrary magnitude.

Figure 1 shows the T dependence of $1/T_1$ measured for three different field directions and $1/T_{2G}$ for $H \parallel c$. We observe that $1/T_1$ is nearly constant above 50 K, while $1/T_{2G}$ increases substantially on cooling. The T dependence of $1/T_{2G}$ can be approximated by $1/\sqrt{T}$ as shown in Fig. 2, where $\sqrt{T}/T_{2G}$ is plotted against temperature with solid dots. These results are consistent with the scaling theory as we discuss below.

In the presence of the hyperfine interaction

$$\mathcal{H} = \sum_{\alpha,i,j} A_\alpha^{ij} I_{i\alpha} S_{j\alpha} \ (\alpha = a, b, \text{ or } c) \tag{1}$$

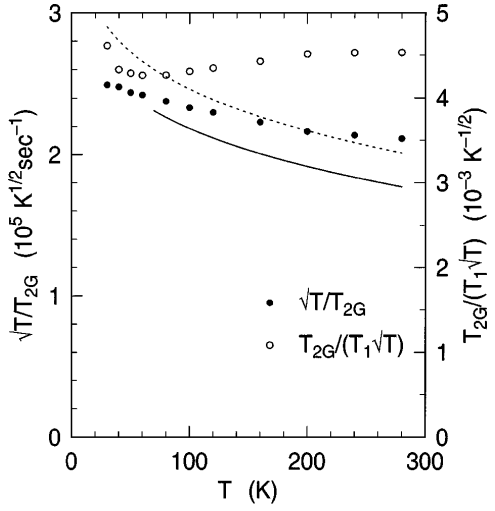

FIG. 2. The T dependencies of $\sqrt{T}/T_{2G}$ (scale on the left axis) and $T_{2G}/T_1\sqrt{T}$ (scale on the right axis) both for $H \parallel c$. The dotted line indicates the $\ln^{1/2}(J/T)$ dependence with arbitrary magnitude. The solid line shows the result of quantum Monte Carlo calculation for $\sqrt{T}/T_{2G}$ by Sandvik without any adjustable parameters.

between a nuclear spin at i site and an electron spin at j site, $1/T_1$ [21] and $1/T_{2G}$ [22,23] are given by the following expressions:

$$\frac{1}{T_1} = \frac{k_B T}{\hbar^2} \int \frac{dq}{2\pi} [A_x^2(q) + A_y^2(q)] \frac{\mathrm{Im}\chi(q,\omega_0)}{\omega_0}, \tag{2a}$$

$$\left(\frac{1}{T_{2G}}\right)^2 = \frac{p}{8\hbar^2}\left[\int \frac{dq}{2\pi} A_z^4(q)\chi^2(q) - \left\{\int \frac{dq}{2\pi} A_z^2(q)\chi(q)\right\}^2\right]. \tag{2b}$$

Here $\chi(q,\omega)$ is the dynamic spin susceptibility in units of $(g\mu_B)^2$, which we assume to be isotropic, $\chi(q) = \mathrm{Re}\chi(q,0)$ is the static susceptibility, ω_0 is the nuclear Larmor frequency, and $A_\alpha(q) = \sum_j A_\alpha^{ij} \exp(iqr_{ij})$. The z axis is the direction of the external field and $p = 0.69$ is the abundance of the ^{63}Cu isotope. Equation (2b) includes only contributions from the z component of the indirect nuclear spin-spin coupling in a static approximation. The mutual spin-flip process caused by the xy components can be neglected in our case because (1) the xy components are small due to the anisotropy of the hyperfine coupling constant as explained below and (2) a reasonably large inhomogeneous linewidth (more than 5 times larger than the homogeneous linewidth) inhibits such a process. Since $1/T_1$ is much smaller than $1/T_{2G}$ for $H \parallel c$, a static approximation is valid [20]. We also note that the nuclear-dipole contribution to $1/T_{2G}$ is negligible.

It was shown [3,24] that $\chi(q,\omega)$ in the 1D $S = 1/2$ Heisenberg model at low temperatures ($T/J \ll 1$) satisfies the following quantum-critical scaling relation for small ω and $q - \pi$ (π is the antiferromagnetic wave vector):

$$\chi(q,\omega) = \frac{1}{T}\tilde{\chi}\left(\frac{c(q-\pi)}{T}, \frac{\hbar\omega}{T}\right), \tag{3}$$

where $c = \pi J/2$ is the spin-wave velocity. This relation implies that both the inverse antiferromagnetic correlation length and the characteristic frequency of the antiferromagnetic spin fluctuations are proportional to T, a situation also encountered at the critical point in the 2D antiferromagnets [7]. The above equations and simple power counting immediately lead to the T dependencies, $1/T_1 \propto 1/c = \text{const}$ and $1/T_{2G} \propto 1/\sqrt{cT}$, which is in agreement with the data. These results are in sharp contrast to the behavior of classical spin chains ($S = \infty$), for which theories predict $1/T_1 \propto 1/T_{2G} \propto T^{-3/2}$ [25,26].

In fact, an accurate analytic expression of $\tilde{\chi}$ is known for the 1D $S = 1/2$ Heisenberg model [3,24], from which the absolute values of the NMR rates are obtained as [8]

$$\frac{1}{T_1} = [A_x^2(\pi) + A_y^2(\pi)]\frac{D}{\hbar J}, \tag{4a}$$

$$\frac{1}{T_{2G}} = \frac{A_z^2(\pi) DI}{4\hbar}\sqrt{\frac{p}{\pi k_B T J}}, \tag{4b}$$

where $I \approx 8.4425$ and D is an unknown constant [27] giving the absolute magnitude of $\chi(q,\omega)$. We have replaced $A(q)$ in Eq. (2) by the value at $q = \pi$ since $\mathrm{Im}\chi(q,\omega)$ and $\chi(q)$ are strongly peaked at $q = \pi$ for $T/J \ll 1$. The unknown constant D cancels out for the ratio

$$\frac{T_{2G}}{T_1\sqrt{T}} = \frac{A_x^2(\pi) + A_y^2(\pi)}{A_z^2(\pi)} \frac{4}{I}\sqrt{\frac{\pi k_B}{pJ}}. \qquad (5)$$

By using Eq. (2a), the anisotropy of the hyperfine coupling constant can be determined from the anisotropy of $1/T_1$ shown in Fig. 1 as $\{A_x^2(\pi) + A_y^2(\pi)\}/A_z^2(\pi) = 2(1/T_1)_z/\{(1/T_1)_x + (1/T_1)_y - (1/T_1)_z\} = 0.203 \pm 0.007$ for $H \parallel c$. For $J = 2200$ K, the right-hand side of Eq. (5) becomes 4.4×10^{-3} K$^{-1/2}$. The ratio $T_{2G}/T_1\sqrt{T}$ for $H \parallel c$ is plotted in Fig. 2 by open circles. It is indeed nearly T independent with the value $(4.3\text{–}4.5) \times 10^{-3}$ K$^{-1/2}$ in excellent agreement with the calculation.

There is a marginally irrelevant operator, however, in the field theory of the 1D $S = 1/2$ Heisenberg model [4,5], which leads to a correction to the above scaling behavior. It was shown that the same operator gives a logarithmic correction to the uniform susceptibility at low temperatures [16], which has indeed been observed in Sr_2CuO_3 [15]. For the NMR rates, Sachdev [8] has shown that this correction leads to an identical mulitiplicative prefactor of $\ln^{1/2}(\Lambda/T)$ to Eq. (4) for both $1/T_1$ and $1/T_{2G}$ to the lowest order in $1/\ln(\Lambda/T)$, where Λ is a high energy cutoff of the order of J. The T dependence $\ln^{1/2}(J/T)$ is shown by the dotted lines in Figs. 1 and 2 with the overall magnitude chosen arbitrarily. It is evident that $1/T_1$ shows much weaker T dependence than $\ln^{1/2}(J/T)$ above 50 K, suggesting that the lowest order correction is not sufficient. At lower temperatures, a steep increase of $1/T_1$ is observed, which may be associated with either the marginally irrelevant operator or the divergence toward 3D ordering at $T_N = 5$ K. The data of $\sqrt{T}/T_{2G}$ show somewhat stronger T dependence than $1/T_1$ but still weaker than $\ln^{1/2}(J/T)$.

So far we have discussed only the T dependence or the ratios of NMR rates. We now turn to the discussion of the absolute values of the rates, which requires the knowledge of hyperfine coupling constants. Since the temperature variation of the susceptibility is very small, the NMR shift (K) is virtually T independent for all directions within the experimental accuracy of ± 50 ppm ($K_a = 0.16\%$, $K_b = 0.18\%$, and $K_c = 0.82\%$). The orbital shift and susceptibility are not known accurately enough to isolate the spin contributions, therefore, the standard K vs χ analysis is not successful. We determined the values of $A(\pi)$ from a structure of the NMR spectra observed below 100 K. The NMR spectra at low temperatures show a broad flat background with fairly sharp edges on both sides, on top of which a sharp peak is observed [28]. From the anisotropy and the T dependence of this structure, we conclude that this is due to a local staggered magnetization near open ends of the spin chains induced by the external field. This phenomenon was first predicted theoretically by Eggert and Affleck [29]. The edges of the spectra correspond to the maximum of the staggered moments located at a finite distance from the chain ends. Detailed discussions of the NMR spectra are presented elsewhere. From the edge positions and the theoretical expression for the magnitude of the staggered moments [29], we obtained $|A_a(\pi)|/2\hbar\gamma_n = 62 \pm 2$, $|A_b(\pi)|/2\hbar\gamma_n = 73 \pm 3$, $|A_c(\pi)|/2\hbar\gamma_n = 220 \pm 10$ kOe, where $\gamma_n = 2\pi \times 1.1285 \times 10^3$ sec^{-1} Oe^{-1} is the nuclear gyromagnetic ratio. We note that the anisotropies of $A(\pi)$ thus determined $A_b(\pi)/A_a(\pi) = 1.18$, $A_c(\pi)/A_a(\pi) = 3.57$ are in good agreement with those estimated from the anisotropy of $1/T_1$, $A_b(\pi)/A_a(\pi) = 1.12$, $A_c(\pi)/A_a(\pi) = 3.4$.

Using the values of $A(\pi)$ and assuming that Eq. (4a) is correct above 60 K, the unknown constant D is determined from the experimental data to be 0.15. A theoretical calculation of D will provide a further consistency check. Sandvik has recently presented QMC calculations of the NMR rates in the 1D $S = 1/2$ Heisenberg model [9]. The results depend on the ratio A^1/A^0, as well as on the values of J and $A_\alpha(\pi)$, where A^0 and A^1 are the anisotropic on-site ($i = j$) and isotropic nearest neighbor ($i = j \pm 1$) coupling, respectively, in the hyperfine Hamiltonian of Eq. (1) [$A(q) = A^0 + 2A^1 \cos q$]. Based on the result that $A^1/2\hbar\gamma_n = 41 \pm 5$ kOe in $YBa_2Cu_3O_x$ [30], we assume that in Sr_2CuO_3 $A^1/2\hbar\gamma_n$ is in the range 30–50 kOe and the $A_\alpha(q)$'s are negative, leading to the value of the ratio $A^1/A_c^0 = -0.2- - 0.4$. Since the QMC results depend little on A^1/A^0 in this range, we can compare them with the experimental data of $1/T_1$ for $H \parallel a$ or b and $1/T_{2G}$ for $H \parallel c$. For $1/T_1$, the QMC result is available only down to $T = J/8 = 280$ K, which is the highest temperature of our measurements. Using the above values of J and $A(\pi)$, the QMC result at $J/T = 8$ gives the value $1/T_1 = 7.73(7.47) \times 10^3$ sec^{-1} for $H \parallel a$ ($H \parallel b$), which is about 40% larger than the experimental data. For $1/T_{2G}$, the QMC calculation is expected to be more accurate and available at lower temperatures. The QMC result for $\sqrt{T}/T_{2G}$ ($H \parallel c$) is shown by the solid line in Fig. 2. Considering that there are no adjustable parameters, agreement with the experimental data is very good, although the QMC result shows a slightly stronger T dependence. [Indeed the T dependence of the QMC result is close to $\ln^{1/2}(J/T)$, as shown by the dotted line.]

It has been known that the long wavelength ($q \sim 0$) spin fluctuations in a Heisenberg magnet show diffusive dynamics at high temperatures, $\mathrm{Im}\chi(q,\omega)/\omega = \chi(q)D_s q^2/\{(D_s q^2)^2 + \omega^2\}$, where D_s is the spin-diffusion constant. In 1D such spin diffusion results in a $1/\sqrt{H}$ magnetic field dependence of $1/T_1$, which has been observed in $(CH_3)_4NMnCl_3$ [26,31], which is an $S = 2/5$ Heisenberg chain, and more recently in $AgVP_2S_6$ [32], which is an $S = 1$ Haldane compound. For $S = 1/2$, however, Sachdev has shown theoretically [8] that the $q \sim 0$ behavior is purely propagating, $\mathrm{Im}\chi(q,\omega)/\omega =$

$\delta(\omega - cq)/4\hbar c$, in the scaling limit. The contribution of these $q \sim 0$ spin fluctuations to $1/T_1$ was shown to be negligibly small compared to the contribution from overdamped spin waves at $q \sim \pi$; see Eq. (4a). In reality, there should be some damping at finite temperatures, leading to a diffusive behavior for very small q, but the spin-diffusion constant is expected to be much larger than the value for a classical Heisenberg system.

We have measured the magnetic field dependence of $1/T_1$ for $H \parallel c$ at $T = 280$ and 50 K as shown in Fig. 3, where $1/T_1$ is plotted against $1/\sqrt{H}$. At $T = 280$ K, a weak field dependence is observed which can be fit by the form $1/T_1 = a + b/\sqrt{H}$. The field dependence becomes even weaker at 50 K. Since the contribution of spin diffusion to $1/T_1$ is expressed as [26]

$$\left(\frac{1}{T_1}\right)_{sd} = [A_x^2(0) + A_y^2(0)] \frac{k_B T \chi(0)}{2\hbar^2 \sqrt{2 g \mu_B D_s H}}, \quad (6)$$

the spin-diffusion constant D_s is determined from the slope of the plot in Fig. 3. At 280 K, where $J\chi(0)/(g\mu_B)^2 = 0.116$ [16], we obtain $D_s = 1 \times 10^{16}$–4×10^{17} sec^{-1}. Although D_s has a large uncertainty due to the ambiguity of the values of $A_\alpha(0)$, it is orders of magnitude larger than the classical value expected in the high temperature limit [26] $(J/\hbar)\sqrt{2\pi S(S+1)/3} = 3.6 \times 10^{14}$ sec^{-1}, which is consistent with the expectation.

In summary, our NMR measurements on a Sr_2CuO_3 single crystal show good quantitative agreement with the scaling theory of the 1D $S = 1/2$ Heisenberg antiferromagnet and the quantum Monte Carlo calculations. The contribution from the $q \sim 0$ spin diffusion was found to be very small.

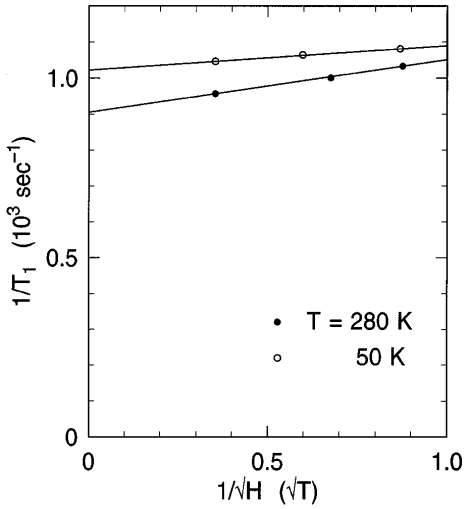

FIG. 3. $1/T_1$ for $H \parallel c$ is plotted against $1/\sqrt{H}$ at two different temperatures.

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