^{17}O NMR Study of $q = 0$ Spin Excitations in a Nearly Ideal $S = \frac{1}{2}$ 1D Heisenberg Antiferromagnet, Sr_2CuO_3, up to 800 K

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We used ^{17}O NMR to probe the uniform (wave vector $q = 0$) electron spin excitations up to 800 K in Sr_2CuO_3 and separate the $q = 0$ from the $q = \pm\frac{\pi}{a}$ staggered components. Our results support the logarithmic decrease of the uniform spin susceptibility below $T \sim 0.015J$, where $J = 2200$ K. From measurement of the dynamical spin susceptibility for $q = 0$ by the spin-lattice relaxation rate $1/T_1$, we demonstrate that the $q = 0$ mode of spin transport is ballistic at the $T = 0$ limit, but has a diffusion-like contribution at finite temperatures even for $T \ll J$.

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The one-dimensional Heisenberg spin chain has one of the simplest Hamiltonians, $H = J\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1}$, yet our understanding of its fascinating quantum mechanical properties is still developing with recent theoretical [1–9] and experimental [10–14] studies. A recent breakthrough in experimental studies of spin chains is the identification of a nearly ideal 1D $S = \frac{1}{2}$ Heisenberg antiferromagnet, Sr_2CuO_3, by Motoyama *et al.* [10]. In this system, $S = \frac{1}{2}$ spins reside at Cu sites, and the superexchange interaction J is mediated by hybridization with the $2p_\sigma$ orbital of the in-chain O(1) site; see Fig. 1(a). Based on the fit of the uniform spin susceptibility $\chi'(q = 0)$ [1], J is estimated to be $J = 2200 \pm 200$ K [10].

Sr_2CuO_3 has proven to be an ideal material for the experimental studies of $S = \frac{1}{2}$ Heisenberg spin chain for various reasons. First and foremost, weak interchain couplings make the temperature of the Néel transition ($T_N = 5$ K) [15] to a three-dimensional long-range ordered state 3 orders of magnitude smaller than J, $T_N = 0.002J$. Thus, the spin excitations of the $S = \frac{1}{2}$ Heisenberg spin chain can be probed at unprecedentedly low scales of temperature and energy. The second major advantage of Sr_2CuO_3 is that ^{63}Cu NMR is observable at the magnetic cation site, because the large J suppresses the nuclear relaxation rates. In a series of publications, Takigawa *et al.* reported detailed ^{63}Cu NMR investigations of the low energy spin excitations [11–13]. They successfully tested the theoretical predictions for the $q = \pm\frac{\pi}{a}$ staggered mode in the scaling limit [2], including the low temperature logarithmic corrections to the staggered dynamical susceptibility [4]. The third major advantage of Sr_2CuO_3, although it has never been exploited in the earlier NMR works, is the high local symmetry of the crystal structure. The Cu-O-Cu chain is strictly straight and the in-chain O(1) site is located in the middle of adjacent Cu sites as shown in Fig. 1(a). Therefore the staggered components of the magnetic hyperfine fields from Cu electron spins are canceled out at the in-chain O(1) sites. Accordingly, one can probe the low energy spin excitations for the $q = 0$ long wavelength mode [see Fig. 1(c)] separately from the staggered $q = \pm\frac{\pi}{a}$ mode. Thus ^{17}O NMR study of Sr_2CuO_3 provides us with a unique opportunity to investigate the $q = 0$ spin excitations down to $T \sim 0.002J$ in the nearly ideal $S = \frac{1}{2}$ Heisenberg spin chain without interference by the staggered mode. Unfortunately, the low oxygen diffusion rate in Sr_2CuO_3 severely limits the ^{17}O isotope enrichment rate, hence the ^{17}O NMR signal intensity. As such, no ^{17}O NMR studies have been reported despite the rich information expected for the unexplored $q = 0$ mode.

In this Letter, we report the first successful ^{17}O NMR investigation of Sr_2CuO_3 single crystals. We accurately measured the temperature dependence of the uniform spin susceptibility $\chi'(q = 0)$ by NMR Knight shift at the in-chain O(1) site *without suffering from the contribution by free spins* that limits the accuracy of bulk susceptibility measurements and ^{63}Cu NMR at low temperatures. We found that $\chi'(q = 0)$ decreases steeply below $T \sim 0.015J$. Our observation supports the presence of a logarithmic decrease of $\chi'(q = 0)$ at low temperatures, but the quantitative agreement with existing theoretical

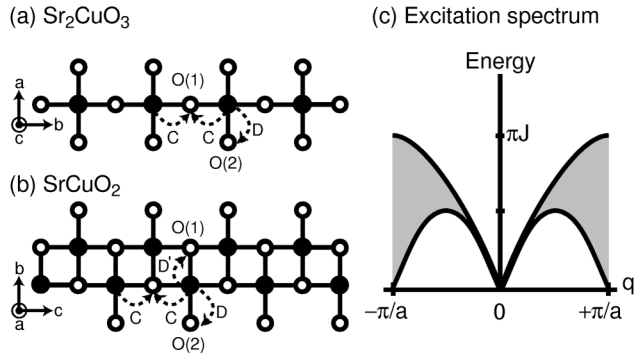

FIG. 1. The fundamental building block of the Cu-O spin chain [Cu (●), O (○)] in (a) Sr_2CuO_3, and (b) a related zigzag spin chain material $SrCuO_2$. Arrows with C, D, and D' ($\sim D$) show the path of transferred hyperfine interactions. (c) The spin excitation spectrum of $S = \frac{1}{2}$ 1D Heisenberg antiferromagnetic spin chain.

models [1] is not good. Based on ^{17}O NMR spin-lattice relaxation rate $1/T_1$, we also test whether the $q = 0$ mode of spin transport is ballistic or diffusive in a $S = \frac{1}{2}$ 1D Heisenberg chain, a long-standing controversy [2,5–9]. Our data strongly support the ballistic nature of spin transport at the $T = 0$ limit, but suggest the presence of diffusion at finite temperatures.

A single crystal of Sr_2CuO_3 was grown in a traveling-solvent floating-zone furnace. ^{17}O isotope was enriched into crystals by annealing them at 900–1045 °C in $^{17}O_2$ gas. NMR measurements were conducted by homemade NMR spectrometers operated typically at 9 T. The hyperfine interaction form factor, F, between ^{17}O nuclear spins and Cu electron spins is represented as $F_1(q) = 2C\cos(\frac{qa}{2})$ and $F_2(q) = D$ at the O(1) and O(2) sites, respectively [16]. C and D represent the hyperfine coupling constant tensor between the observed ^{17}O nuclear spin and the nearest neighbor Cu electron spins, as schematically shown in Fig. 1(a). We determined the hyperfine coupling tensor based on the standard K-χ plot analysis as $2C^a = 45$, $2C^b = 95$, $2C^c = 44$, $D^a = 75$, $D^b = 23$, $D^c = 14 \pm 10$ kOe/μ_B. The superscripts represent the crystal axes. One kOe/μ_B is a hyperfine interaction of $g\gamma_n\hbar = 4.74 \times 10^{-9}$ eV for ^{17}O, where $\gamma_n = 5.772$ MHz/T is the nuclear gyromagnetic ratio.

In Fig. 2, we present the temperature dependence of the NMR Knight shift $K^a(1)$ measured at the in-chain O(1) site with 9 T of uniform magnetic field applied along the a axis. We emphasize that one cannot achieve such extremely high experimental accuracy at the O(2) and Cu sites at low temperatures, because the enhanced staggered spin susceptibility near $q = \pm\pi/a$ causes both homogeneous line broadening as well as inhomogeneous line broadening arising from defects [13]. In contrast $F_1(q = \pm\frac{\pi}{a}) = 0$ implies that these line-broadening mechanisms are ineffective at the in-chain O(1) sites, and the linewidth remains 1 to 2 orders of magnitude narrower than at the O(2) and Cu sites. The O(1) linewidth is only 8 kHz at 30 K, compared to 50 kHz for the O(2) linewidth. The NMR shift $K^a(1)$ can be expressed as

$$K^a(1) = \frac{2C^a}{N_A\mu_B}\chi'(q = 0) + K^a_{VV}(1). \qquad (1)$$

where the first term [$K^a_{\rm spin}(1)$ in Fig. 2] arises from the uniform spin susceptibility $\chi'(q = 0)$, while the second term $K^a_{VV}(1) = 0.024\%$ represents the small temperature independent contribution of the Van-Vleck term as determined by the K-χ plot analysis. The temperature dependence above 30 K of $\chi'(q = 0)$ can be fitted very well with the high temperature theory [10,17]. Below 30 K ($\sim 0.015J$), $\chi'(q = 0)$ begins to decrease steeply. We may compare the steep decrease of $\chi'(q = 0)$ with the theoretical prediction by Eggert, Affleck, and Takahashi [1] based on conformal field theory. They predicted a logarithmic term which has a steep decrease with an infinite slope at the zero temperature limit, $J\pi^2\chi'(q = 0) \sim 1 + \frac{1}{2\ln(T_o/T)}$ with $T_o \sim 7.7J$, as shown in Fig. 3(c). At the qualitative level, our data support the presence of a steep decrease of $\chi'(q = 0)$. However, our results show that the theoretically predicted logarithmic term in $\chi'(q = 0)$ does not account for our low temperature experimental results at the quantitative level [see Fig. 3(c)]. We note that Motoyama *et al.* [10] earlier concluded that their bulk susceptibility measurements matched the theoretical result above $\sim$10 K. However, we

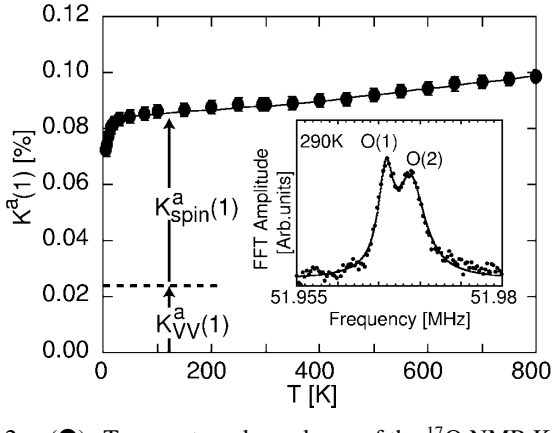

FIG. 2. (●): Temperature dependence of the ^{17}O NMR Knight shift $K^a(1)$ measured at the in-chain O(1) sites in Sr_2CuO_3. The solid curve represents analytic calculations by M. Takahashi *et al.* for $J = 2200$ K, $2C^a = 45$ kOe/μ_B, and $K^a_{VV} = 0.024\%$. Inset: The FFT NMR line shape of ^{17}O central transitions in Sr_2CuO_3 observed at 290 K. The solid line is a best fit.

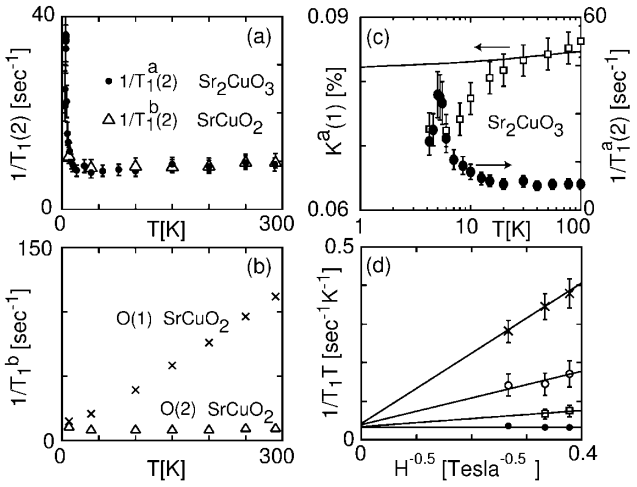

FIG. 3. (a) and (b): $1/T_1^a(2)$ in Sr_2CuO_3 (●), $1/T_1^b(2)$ in $SrCuO_2$ (△), and $1/T_1^b(1)$ in $SrCuO_2$ (×). (c) The same data of $1/T_1^a(2)$ (●) in Sr_2CuO_3 is compared with $K^a(1)$ (□) in a semilog scale. The solid curve is the theoretically predicted logarithmic form for $K^a(1)$. (d) Frequency dependence of $1/T_1^a(1)T$ in Sr_2CuO_3 at 77 K (□) and 295 K (○), $1/T_1^a(2)T$ in Sr_2CuO_3 at 295 K (●), and $[1/T_1^b(1)T - 1/T_1^b(2)T]$ in $SrCuO_2$ at 295 K (×). The $1/\sqrt{H} = 1/\sqrt{\omega_n} = 0$ limit is the theoretical estimate of $1/T_1^{q=0}(1)T + 1/T_1^{q=\pm\pi/a}(1)T$. Solid lines are the best linear fit with the theoretical constraint at $1/\sqrt{H} = 0$. For a contribution from spin diffusion, the slope is proportional to $1/\sqrt{D_s}$.

emphasize that our ^{17}O NMR Knight shift data do not suffer from the Curie term observed in the bulk susceptibility data. As already pointed out by Motoyama *et al.* [10], the necessity of subtracting the Curie term $\sim 1/T$ with a divergently large *negative* temperature coefficient from the bulk susceptibility data leaves ambiguities in the temperature dependence of the potential logarithmic term deduced after the subtraction, because the latter has a divergently large *positive* temperature coefficient. In contrast, $K^a(1)$ directly reflects the local spin susceptibility $\chi'(q = 0)$ of the neighboring Cu electron spins and has no such ambiguity. Thus the results in Fig. 2 provide an unambiguous experimental test for theories.

We also measured the temperature dependence of the ^{17}O nuclear spin-lattice relaxation rate $1/T_1^a(2)$ at the O(2) site as presented in Figs. 3(a), 3(c), and 4(a). $1/T_1^a$ at O(1) and O(2) sites may be expressed as

$$\frac{1}{T_1^a} = \frac{\gamma_n^2 k_B T}{\mu_B^2} \sum_q [|F^b(q)|^2 + |F^c(q)|^2] \frac{\chi''(q, \omega_n)}{\omega_n}, \quad (2)$$

where ω_n ($\sim \gamma_n H$) is the resonance frequency. Since the form factor at the O(2) site $F_2(q)$ is independent of wave vector q, $1/T_1(2)$ at the O(2) sites measures the wave vector q integral of $\chi''(q, \omega_n)$. This represents the strength of the low frequency (ω_n) Cu electron spin fluctuations. The roughly constant value of $1/T_1(2)$ at high temperatures reflects the cancellation of the two temperature dependent parts of Eq. (2), $1/T_1 \propto T$ which offsets the $\sim 1/T$ increase of the q integral of the staggered spin susceptibility $\chi''(q = \pm\frac{\pi}{a}, \omega_n)$, as previously reported by Takigawa *et al.* [11] and Thurber *et al.* [18] based on ^{63}Cu NMR. We note that the mild increase of $1/T_1(2)$ down to ~ 12 K is consistent with the logarithmic correction intrinsic to 1D behavior [11]. We recall that the onset of a steep decrease of $\chi'(q = 0)$ is evident in our $K^a(1)$ data already below ~ 30 K as shown in Fig. 3(c). This suggests that the decrease of $\chi'(q = 0)$ is a property of the 1D spin chains rather than the 3D short-range order effects. However, $1/T_1(2)$ strongly increases below ~ 12 K, and diverges at $T_N = 5.2$ K. This indicates that three-dimensional short-range order is the dominant factor of the strong decrease of $\chi'(q = 0)$ in the same temperature range below ~ 12 K. In addition, we cannot rule out the possibility that the discrepancy between theory and experiment is caused by the finite length of the spin chains caused by defects. The finite chain length produces a staggered ($q = \pm\frac{\pi}{a}$) spin density oscillation in this temperature regime [13] which might cause unknown effects to the temperature dependence of $\chi'(q = 0)$.

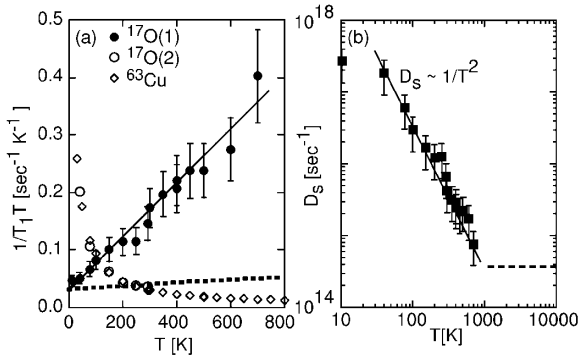

FIG. 4. (a) $1/T_1^a T$ for in-chain O(1) (●), and O(2) (○), and $1/T_1^c T$ for ^{63}Cu [(◇), divided by a factor of 112] in Sr_2CuO_3. The solid line is the best empirical fit to O(1), $1/T_1^a(1)T = 0.027 + 4.7 \times 10^{-4} T$ sec^{-1} K^{-1}. The dashed line represents the scaling limit estimate of $1/T_1^{a,q=0}(1)T + 1/T_1^{a,q=\pm\pi/a}(1)T$. (b) Temperature dependence of the spin diffusion constant D_s deduced from $1/T_1^a(1)T$. This deduced value represents a lower bound on the spin diffusion constant. The high temperature limit, $D_s = (J/\hbar)\sqrt{2\pi S(S+1)/3} = 3.6 \times 10^{14}$ sec^{-1}, is also shown by a dashed line.

Next we turn our attention to the temperature dependence of the long wavelength $q = 0$ mode of the low frequency Cu electron spin fluctuations. The temperature dependence of $1/T_1^a T$ at the in-chain O(1) and apical O(2) sites is compared in Fig. 4(a). We found that $1/T_1^a(1)T$ may be approximated by an empirical form, $1/T_1^a(1)T = 0.027 + 4.7 \times 10^{-4} T$ sec^{-1} K^{-1} at low temperatures. $1/T_1^a(1)T$ shows qualitatively different behavior from $1/T_1^a(2)T$, because the hyperfine form factor $F_1(q = \pm\frac{\pi}{a}) = 0$ *filters out* the contribution of the staggered susceptibility and $1/T_1^a(1)T$ is dominated by $q \sim 0$ [see Fig. 1(c)]. According to the theoretical prediction by Sachdev [2] based on quantum critical scaling at the low temperature limit, the $q = 0$ contribution to $1/T_1^a(1)T$ may be written as $1/T_1^{a,q=0}T = [(2C^b)^2 + (2C^c)^2] g^2 \gamma_n^2 \hbar k_B / \pi^3 J^2$. The underlying assumption is that the $q = 0$ spin excitations propagate ballistically without damping at low temperatures rather than diffusive transport. By inserting C^b, C^c, and J into the scaling form, we obtain the theoretical estimate of the contribution by the undamped ballistic mode, $1/T_1^{a,q=0}(1)T = 0.029 \pm 0.006$ sec^{-1} K^{-1}. This is in excellent agreement with our experimental zero temperature limit, $1/T_1^a(1)T = 0.027 \pm 0.004$ sec^{-1} K^{-1} without any adjustable parameters. We note that the contribution by the $q = \pm\frac{\pi}{a}$ branch, $1/T_1^{q=\pm\pi/a}(1)T$ is not negligible at $T \neq 0$, because the form factor $F_1(q)$ will be finite for any $q \neq \pm\frac{\pi}{a}$. However, by integrating the wave vector dependent scaling form of the staggered susceptibility [2] convoluted by the form factor $|F_1(q)|^2$, we estimate $1/T_1^{q=\pm\pi/a}(1)T$ as only $\sim 5\%$ of the observed rate at 300 K, and the percentage contribution decreases slowly with decreasing temperature. Thus the scaling estimation of the sum of the two separate modes of contributions, $1/T_1^{q=0}(1)T + 1/T_1^{q=\pm\pi/a}(1)T$, while providing a very good estimate for $T = 0$, severely underestimates our experimental results *at any finite temperature,* as shown by a dashed line in Fig. 4(a). Moreover, we found that $1/T_1(1)$ depends on frequency as shown in Fig. 3(d).

Thus, there is an additional contribution to the low energy spin susceptibility for $q \sim 0$ that increases strongly

with increasing temperature and decreasing frequency. This suggests that spin diffusion [19] is important, even for $T \ll J$. We measured the frequency dependence of $1/T_1(1)$ between $H = 7$ T ($\omega_n = \gamma_n H = 40.4$ MHz) and $H = 14$ T ($\omega_n = 80.8$ MHz) at 77 and 295 K. The mild frequency dependence of $1/T_1(1)$ presented in Fig. 3(d) is consistent with the $1/\sqrt{\omega_n}$ dependence [20] expected for the diffusive contribution,

$$\frac{1}{T_1^{\mathrm{diff},a} T} = [(2C^b)^2 + (2C^c)^2] \frac{\gamma_n^2 k_B \chi'(q=0)}{2\mu_B^2 \sqrt{2\omega_e D_s}}, \quad (3)$$

where $\omega_e = g\mu_B H/\hbar \propto \omega_n$. The ^{63}Cu NMR $1/T_1$ [11] also had a small frequency dependent component consistent with $1/\sqrt{\omega_n}$, even though Cu NMR is dominated by the $q = \pm\frac{\pi}{a}$ modes. $1/T_1(2)T$ for the O(2) sites does not have any frequency dependence within error, indicating that the dominant $q = \pm\frac{\pi}{a}$ modes are not diffusive. To further establish the presence of an unexpectedly large diffusive contribution in the $S = \frac{1}{2}$ Heisenberg spin chain, we also measured $1/T_1(1)$ in a related one-dimensional spin chain system $SrCuO_2$ [see Figs. 1(b) and 3(b)]. Since the signal intensity of ^{17}O NMR is strong in $SrCuO_2$ owing to the higher isotope enrichment rate, we could measure the frequency dependence of $1/T_1(1)$ with higher accuracy. Because of the transferred hyperfine coupling $D'(\sim D)$ from the adjacent chain, to a good approximation $1/T_1(1)$ in $SrCuO_2$ is a superposition of the contributions from the $q = 0$ modes and $1/T_1(2)$. This explains why $1/T_1(1)$ in $SrCuO_2$ asymptotes to $1/T_1(2)$ at the low temperature limit as shown in Fig. 3(b). The presence of a large contribution with $1/\sqrt{\omega_n}$ dependence is clearly seen in Fig. 3(d).

Theoretically, even whether spin diffusion exists for the $q = 0$ mode of the $S = \frac{1}{2}$ 1D Heisenberg spin chain is controversial [2,5–9]. Spin diffusion has been measured by NMR in $S = \frac{5}{2}$ spin chains [20] and a $S = 1$ Haldane-gap system [21], but to our knowledge not for a $S = \frac{1}{2}$ system. Quantum Monte Carlo results [3,5] indicate a strong increase (faster than T) of $1/T_1(q = 0)$ with temperature, but do not determine if the $q = 0$ peak is truly diffusive. Fabricius and McCoy [6] have calculated that the frequency dependence may be $\sim\omega^{-0.3}$ rather than $\omega^{-0.5}$, while a finite size scaling analysis suggests ballistic behavior [7]. Our ^{17}O $1/T_1$ results clearly show frequency dependence, but are not accurate enough to conclusively distinguish the exact exponent. If we assume that the extra contribution to $1/T_1T$ is genuinely diffusive with frequency dependence $\omega^{-0.5}$, we can estimate the temperature dependence of the spin diffusion constant D_s, which is the only unknown parameter in Eq. (3). In such a scenario, $D_s \sim 1/T^2$ for $T \ll J$ as shown in Fig. 4(b). We caution, however, that this estimate of D_s is a lower bound on the value, since we are assuming that the additional contribution to T_1 is entirely diffusive.

To conclude, we have successfully separated the $q = 0$ mode in both static and dynamic spin susceptibility in a nearly ideal 1D $S = \frac{1}{2}$ Heisenberg antiferromagnet material. We unambiguously demonstrated a steep decrease below $T = 0.015J$ of $\chi'(q = 0)$. Measurements of the low frequency $q \sim 0$ dynamic spin susceptibility have a $T = 0$ limit that agrees with purely ballistic spin transport. However, with increasing temperature, the dynamic spin susceptibility strongly increases. This result establishes the presence of nonballistic behavior at finite temperatures, even for $T \ll J$. We suggest the increased dynamic spin susceptibility is from diffusive contributions, and estimated a lower bound on the diffusion constant $D_s \sim 1/T^2$. Whether these new results can be accounted for by the one-dimensional $S = \frac{1}{2}$ Heisenberg model remains to be seen.

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