

17O NMR study of \( q = 0 \) spin excitations in a nearly ideal \( S = \frac{1}{2} \) 1D Heisenberg antiferromagnet, Sr\(_2\)CuO\(_3\), up to 800 K

K.R. Thurber,\(^{1,2}\) A.W. Hunt,\(^{1,2}\) T. Inai,\(^{1,2}\) and F.C. Chou\(^2\)

Department of Physics\(^3\) and Center for Materials Science and Engineering,\(^2\) M.I.T., Cambridge, MA 02139

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We used 17O NMR to probe the uniform (wavevector \( q = 0 \)) electron spin excitations up to 800 K in Sr\(_2\)CuO\(_3\) 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 \( T \sim 0.015 J \), 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 \( T \ll J \).

The one-dimensional Heisenberg spin chain has one of the simplest Hamiltonians, \( H = J \sum_i S_i \cdot S_{i+1} \), yet our understanding of its fascinating quantum mechanical properties is still developing with recent theoretical\(^{[1–8]}\) and experimental\(^{[9–12]}\) studies. A recent breakthrough in experimental studies of spin chains is the identification of a nearly ideal 1D \( S = \frac{3}{2} \) Heisenberg antiferromagnet, Sr\(_2\)CuO\(_3\), by Motoyama et al.\(^{[9]}\) In this system, \( S = \frac{3}{2} \) 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.\(^{[2]}\)

Sr\(_2\)CuO\(_3\) has proven to be an ideal material for the experimental studies of \( S = \frac{3}{2} \) Heisenberg spin chain for various reasons. First and foremost, weak inter-chain couplings make the temperature of the Néel transition \( (T_N = 5K) \)\(^{[3]} \) to a three-dimensional long-range ordered state three orders of magnitude smaller than \( J \), \( T_N = 0.002 J \). Thus, the spin excitations of the \( S = \frac{3}{2} \) Heisenberg spin chain can be probed at unprecedentedly low scales of temperature and energy. The second major advantage of Sr\(_2\)CuO\(_3\) is that \( \Delta \)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 \( \Delta \)Cu NMR investigations of the low energy spin excitations\(^{[10–12]}\). They successfully tested the theoretical predictions for the \( q = \pm \frac{\pi}{a} \) staggered mode in the scaling limit\(^{[3]} \), including the low temperature logarithmic corrections to the staggered dynamical susceptibility\(^{[4]} \). The third major advantage of Sr\(_2\)CuO\(_3\), 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 wave-length mode (see Fig.1(c)) separately from the staggered \( q = \pm \frac{\pi}{a} \) mode. Thus 17O NMR study of Sr\(_2\)CuO\(_3\) provides us with a unique opportunity to investigate the \( q = 0 \) spin excitations down to \( T \sim 0.002 J \) in the nearly ideal \( S = \frac{3}{2} \) Heisenberg spin chain without interference by the staggered mode. Unfortunately, the low oxygen diffusion rate in Sr\(_2\)CuO\(_3\) severely limits the 17O isotope enrichment rate, hence the 17O NMR signal intensity. As such, no 17O NMR studies have been reported despite the rich information expected for the unexplored \( q = 0 \) mode.

In this Letter, we report the first successful 17O NMR investigation of Sr\(_2\)CuO\(_3\) 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 \( \Delta \)Cu NMR at low temperatures. We found that \( \chi'(q = 0) \) decreases steeply below \( T \sim 0.015 J \) without the signature of three-dimensional short range order approaching the Néel state. Our observation supports the presence of a logarithmic decrease of \( \chi'(q = 0) \) at low temperatures, but the quantitative agreement with existing theoretical models\(^{[3]}\) is not good. Based on 17O 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 \( S = \frac{3}{2} \) 1D Heisenberg chain, a long standing controversy\(^{[3,4]}\). Our data strongly support the ballistic nature of spin transport at the \( T \sim 0 \) limit, but suggest the presence of diffusion at finite temperatures.

A single crystal of Sr\(_2\)CuO\(_3\) was grown in a traveling-solvent floating-zone furnace. 17O isotope was enriched into crystals by annealing them at 900-1045 C in 17O\(_2\) gas. NMR measurements were conducted by home made NMR spectrometers operated typically at 9 Tesla. The hyperfine interaction form factor, \( F \), between 17O nuclear spins and Cu electron spins is represented as \( F_1(q) = 2C \cos(q\frac{\pi}{a}) \) and \( F_2(q) = D \) at the O(1) and O(2) sites, respectively\(^{[3]}\). \( C \) and \( D \) represent the hyperfine coupling constant tensor between the observed 17O 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 $K - \chi$ plot analysis as $2C^a = 45$, $2C^b = 95$, $2C^c = 44$, $D^a = 75$, $D^b = 29$, $D^c = 14 \pm 10 \text{kOe}/\mu_B$. The superscripts represent the crystal axes. One kOe/$\mu_B$ is a hyperfine interaction of $g\gamma_n \hbar = 4.74 \times 10^{-9} \text{eV}$ for $^{17}$O.

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 Tesla 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 in 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 [12]. In contrast, homogeneous line broadening as well as inhomogeneous line broadening arising from defects in the zero temperature limit, the term which has a steep decrease with an infinite slope at $q(1) = 2\pi/a$, is a property of the 1D system intrinsic to 1D behavior [10]. Only at the lowest temperature measured (4.2 K) does $1/T_1(2)$ strongly increase, indicating the three-dimensional order of the Néel state at $T_N = 5 \text{K}$. We emphasize that the effect of three-dimensional short range order is not seen in $1/T_1(2)$ for the region 30 K down to 10 K, where a steep decrease of $\chi'(q = 0)$ is evident in our $K^a(1)$ data. This implies that the decrease of $\chi'(q = 0)$ is a property of the 1D spin chains, not a 3D ordering effect. On the other hand, 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 ($q = \pm \pi/a$) spin density oscillation in this temperature regime [12] which might cause unknown effects to $\chi'(q = 0)$.

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 $1/T_1(2)T$ at the in-chain O(1) and apical O(2) sites is compared in Fig.4(a). We found that $1/T_1^0(1)T$ may be approximated by an empirical form, $1/T_1^0(1)T = 0.027 + 4.7 \times 10^{-4} T \text{sec}^{-1} \text{K}^{-1}$ at low temperatures. $1/T_1^0(2)T$ shows qualitatively different behavior from $1/T_1^0(2)T$, because the hyperfine form factor $F_1(q = \pm \pi/a) = 0$ filters out the contri-
bution of the staggered susceptibility and $1/T_1^\alpha(1)$ 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 $1/T_1^\alpha(1)$ may be written as $1/T_1^\alpha(q=0,T) = [(2C^b)^2 + (2C^c)^2]^{1/2} \gamma_n^2 \mu_B B / \pi^3 J^2$. 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, $1/T_1^\alpha(q=0,T) = 0.029 \pm 0.006$ sec$^{-1}$K$^{-1}$. This is in excellent agreement with our experimental zero temperature limit, $1/T_1^\alpha(1)T = 0.027 \pm 0.004$ sec$^{-1}$K$^{-1}$ without any adjustable parameters. We note that the contribution by the $q = \pm \frac{\pi}{a}$ branch, $1/T_1^\alpha(q=\pm \frac{\pi}{a},T)$ is not negligible at $T \neq 0$, because the form factor $F(q)$ will be finite for any $q \neq \pm \frac{\pi}{a}$. However by integrating the wave-vector dependent form of the staggered susceptibility [2] convoluted by the form factor $|F(q)|^2$, we estimate $1/T_1^\alpha(q=\pm \frac{\pi}{a},T)$ 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, $1/T_1^\alpha(q=0,T) + 1/T_1^\alpha(q=\pm \frac{\pi}{a},T)$, 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. Moreover, we found that $1/T_1(1)$ depends on frequency as shown in Fig. 3(c).

Thus, there is an additional contribution to the low energy spin susceptibility for $q = 0$ that increases strongly with increasing temperature and decreasing frequency. This suggests that spin diffusion [7] is important, even for $T \ll J$. We measured the frequency dependence of $1/T_1(1)$ between $H = 7$ Tesla ($\omega_n = \gamma_n H = 40.4$ MHz) and $H = 14$ Tesla ($\omega_n = 80.8$ MHz) at 77 K and 295 K. The mild frequency dependence of $1/T_1(1)$ presented in Fig.3(c) is consistent with the $1/\sqrt{\omega_n}$ dependence [18] expected for the diffusive contribution,

$$\frac{1}{T_1^{\text{diff},\alpha}} = [(2C^b)^2 + (2C^c)^2]^{1/2} \gamma_n^2 \mu_B B \chi'(q = 0) 2 \mu_B^2 \sqrt{2\omega_n} D_s$$

where $\omega_c = g \mu_B H / \hbar \propto \omega_n$. The $^{63}$Cu NMR $1/T_1$ [10] 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 Fig.1(b) and Fig.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(c).

Theoretically, even whether spin diffusion exists for the $q = 0$ mode of the $S = \frac{1}{2}$ 1D Heisenberg spin chain is controversial [2,3-8]. Spin diffusion has been measured by NMR in $S = \frac{1}{2}$ spin chains [13] and a $S = 1$ Haldane-gap system [19], but to our knowledge not for a $S = \frac{1}{2}$ system. Quantum Monte Carlo results [6,8] indicate that the frequency dependence may be $\sim \omega^{-3/2}$ rather than $\omega^{-5/2}$, while a finite size scaling analysis suggests ballistic behavior [3]. 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 $1/T_1$ is genuinely diffusive with frequency dependence $\omega^{-5/2}$, we can estimate the temperature dependence of the spin diffusion constant $D_s$, which is the only unknown parameter in eq.(1). 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 non-ballistic 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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* Current address: US Army Research Lab, Adelphi, MD.
[1] S. Eggert, I. Affleck, and M. Takahashi, Phys. Rev. Lett. 73, 332 (1994).
A. Keren et al., Phys. Rev. B 50, 13006 (1994).
[3] A.W. Sandvik, Phys. Rev. B 52, R9381 (1995).
[4] O.A. Starykh, R. P. Singh, and A.W. Sandvik, Phys. Rev. Lett. 78, 539 (1997).
[5] O.A. Starykh, A.W. Sandvik, and R. P. Singh, Phys. Rev. B 55, 14953 (1997).
[6] K. Fabricius and B.M. McCoy, Phys. Rev. B 57, 8340 (1998) and references therein.
[7] B.N. Narozhny, A.J. Millis, and N. Andrei, Phys. Rev. B 58, R2921 (1998).
[8] C. Buragohain and S. Sachdev, Phys. Rev. B 59, 9285 (1999).
[9] N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. 76, 3212 (1996).
[10] M. Takigawa et al., Phys. Rev. Lett. 76, 4612 (1996).
[11] M. Takigawa et al., Phys. Rev. B 56, 13681 (1997).
[12] M. Takigawa et al., Phys. Rev. B 55, 14129 (1997).
[13] A. Keren et al., Phys. Rev. B 48, 12926 (1993); K.M. Kojima et al., Phys. Rev. Lett. 78, 1787 (1997).
[14] T. Moriya, J. Phys. Soc. Jpn. 18, 516 (1963).
[15] M. Takahashi and T. Sakai, Haldane Magnets and Related 1D Magnets: Properties in Magnetic Field in Computational Physics as a New Frontier in Condensed Matter Research, edited by H. Takayama, et al., Phys. Soc. of Japan (1995).
[16] K.R. Thurber et al., Phys. Rev. Lett. 84, 558 (2000).
[17] P.G. deGennes in Magnetism, edited by G. Rado and H. Suhl (Academic, New York, 1963), Vol. 3, p. 115.
[18] F. Borsa and M. Mali, Phys. Rev. B 9, 2215 (1974).
[19] M. Takigawa et al., Phys. Rev. Lett. 76, 2173 (1996).

FIG. 1. The fundamental building block of the Cu-O spin chain (Cu •, O ◦) in (a) Sr₂CuO₃, and (b) a related zig-zag spin chain material SrCuO₂. Arrows with C, D, and D′ (∼D) show the path of transferred hyperfine interactions. (c) The spin excitation spectrum of $S = \frac{1}{2}$ 1D Heisenberg antiferromagnetic spin chain.

FIG. 2: •: Temperature dependence of the $^{17}$O NMR Knight shift $K^{n}(1)$ measured at the in-chain O(1) sites in Sr₂CuO₃. Solid curve represents analytic calculations of uniform spin susceptibility $\chi'(q=0)$ by M. Takahashi et al. for $J = 2200$ K, $2C' = 45$ kOe/$\mu_B$, and $K_{V,V}^y = 0.024%$. Inset: The same data in an extended scale. The solid curve is the theoretically predicted logarithmic form.

FIG. 3. (a) and (b): $1/T_{1}^{n}(2)$ in Sr₂CuO₃ (●), $1/T_{1}^{n}(2)$ in SrCuO₂ (∆), and $1/T_{1}^{n}(1)$ in SrCuO₂ (×). (c) Frequency dependence of $1/T_{1}^{n}(1)T$ in Sr₂CuO₃ at 77K (◼) and 295 K (○), $1/T_{1}^{n}(2)T$ in Sr₂CuO₃ at 295 K (●), and $(1/T_{1}^{n}(1)T - 1/T_{1}^{n}(2)T)$ in SrCuO₂ at 295 K (X). The $1/\sqrt{H} = 1/\sqrt{\omega_{n}} = 0$ limit is the theoretical estimate of $1/T_{1}^{n=0}(1)T + 1/T_{1}^{n=\pm \pi}(1)T$. 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 $1/\sqrt{D_s}$.
(a) \( \text{Sr}_2\text{CuO}_3 \)

(b) \( \text{SrCuO}_2 \)

(c) Excitation spectrum

\[ -\frac{\pi}{a} \quad 0 \quad +\frac{\pi}{a} \]

\[ \text{Energy} \]

\[ \pi J \]
(a) \( \frac{1}{T_1 T} \) vs. \( T \) [K]

(b) \( D_s \sim \frac{1}{T^2} \)