Magnetic properties of the triangular quantum spin tube \([(\text{CuCl}_2\text{tachH})_3\text{Cl}]\text{Cl}_2\) studied by NMR and magnetization

Yuji Furukawa\textsuperscript{1,2}, Yuzuru Sumida\textsuperscript{2}, Ken-ichi Kumagai\textsuperscript{2}, Ferdinando Borsa\textsuperscript{1,3}, Hiroyuki Nojiri\textsuperscript{1}, Yusei Shimizu\textsuperscript{2}, Hiroshi Amitsuka\textsuperscript{2}, Ken-ichi Tenya\textsuperscript{5}, Paul Kögerler\textsuperscript{1,6}, Leroy Cronin\textsuperscript{7}

\textsuperscript{1}Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA

\textsuperscript{2}Department of Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

\textsuperscript{3}Departmento Fisica “A. Volta”, Universita di Pavis, Via Bassi 6, I27100 Pavia, Italy

\textsuperscript{4}Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan

\textsuperscript{5}Department of Physics, Faculty of Education, Shinshu University, Nagano 380-8544, Japan

\textsuperscript{6}Institute of Inorganic Chemistry, RWTH Aachen University, 52074 Aachen, Germany

\textsuperscript{7}Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK

E-mail: furukawa@ameslab.gov

Abstract. Static and dynamical properties of Cu\textsuperscript{2+} \((3d^{9}; S = 1/2)\) spins in a twisted Heisenberg triangular spin tube, \([(\text{CuCl}_2\text{tachH})_3\text{Cl}]\text{Cl}_2\), have been investigated by nuclear magnetic resonance (NMR) and magnetization measurements in the temperature range \(T = 0.05\)\textendash300 K. Magnetization curves below 0.5 K show a clear change in slope around 5 T, attributed to a signature of 1/3 plateau in magnetization. From a systematic measurement of nuclear spin-lattice relaxation rates as a function of temperature and external field, the fluctuation frequency of Cu\textsuperscript{2+} spins is found to decrease with decreasing temperature, revealing an unusual slow spin dynamics at low temperatures.

1. Introduction
Magnetic properties of geometrically frustrated antiferromagnets have been attracted a great deal of interest, due to pronounced quantum phenomena, such as the suppression of the magnetic ordering and unconventional spin state like e.g. spin liquid [1]. Of particular interest is a new one-dimensional quantum spin system composed of one-dimensional arrays of Heisenberg triangular antiferromagnets,

Published under licence by IOP Publishing Ltd
called a triangular spin tube. Each Heisenberg antiferromagnetic triangle has a geometrical spin frustration effect so that the system has a new degree of freedom, spin chirality [2], in addition to the one-dimensional spin nature. Recent theoretical studies [3-6] indicate possible new quantum phenomena like a Tomonaga-Luttinger liquid state with spin chirality and spin gap formation, due to spin chirality in the quantum triangular spin tube.

\[(\text{CuCl}_2\text{tachH})_3\text{Cl}]\text{Cl}_2 \text{ (tach=cis,trans-1,3,5-triamino-cyclohexane)}, \] is a newly synthesized triangle spin tube [7]. With a trigonal crystal structure (space group P6\_3/m, lattice parameters \(a = b = 12.800 \text{ Å}, c = 12.6287 \text{ Å}\))[7], the triangles formed by three \(\text{Cu}^{2+} (3d^9, S = 1/2)\) ions are aligned to construct infinite stacks of one-dimensional antiprisms along the \(c\) direction. A schematic structure of the triangular copper chain is shown in Fig. 1. Each triangle rotates 180 degrees with respect to its neighboring triangles in the chain direction. From the temperature dependence of magnetic susceptibility measured between 2 and 300 K, antiferromagnetic interactions intra-triangle and inter-triangle are reported as \(J_1/k_B \approx 0.9 \text{ K}\) and \(J_2/k_B \sim 1.95 \text{ K}\) [8], respectively. Although initially the system was reported to have a spin singlet ground state with a spin gap \(\Delta/k_B \sim 0.4 \text{ K}\) [8] from a magnetization curve at temperature \(T = 0.5 \text{ K}\), theoretical investigations indicate a gapless ground state for the twisted triangular spin tube [5-7]. Experimentally, a gapless ground state of the Cu spin tube was revealed by the observation of proton NMR line broadening at temperatures below 1 K [9]. Quite recently, specific heat measurements down to 100 mK also evidenced a gapless ground state of the Cu spin tube from the observed \(T\) linear dependence of the specific heat below 0.6 K, which is attributed to a Tomonaga-Luttinger liquid state [10].

In this paper, we report our results of the magnetization and proton NMR measurements at very low temperatures, down to 100 mK, using a \(^3\text{He}-\)\(^4\text{He}\) dilution refrigerator. A change in slope of the magnetization curve around 5 T provides first evidence of \(1/3\) plateau in the magnetization. Nuclear spin lattice relaxation rate, \(1/T_1\), reveals a peculiar slow spin dynamics of the \(\text{Cu}^{2+}\) spins in the system.

FIG 1. Schematic structure of the triangular spin tube, \([\text{CuCl}_2\text{tachH}]_3\text{Cl}]\text{Cl}_2\). The circles show \(\text{Cu}^{2+}\) (S = 1/2) ions. The blue and grey lines correspond to the intra-triangle exchange \((J_1/k_B \sim 0.9 \text{ K})\) and inter-triangle exchange \((J_2/k_B \sim 1.95 \text{ K})\) coupling paths.

2. Experimental
Polycrystalline samples of \([\text{CuCl}_2\text{tachH}]_3\text{Cl}]\text{Cl}_2\) were prepared as described in Ref. [7]. The temperature dependence of the magnetic susceptibility was measured in a temperature range of 1.8-300 K using a superconducting quantum interface device (SQUID) magnetometer (Quantum design MPMS-7T). DC magnetization measurements below 1 K were performed using a Faraday force capacitive magnetometer installed in the \(^3\text{He}-\)\(^4\text{He}\) dilution refrigerator. The \(^1\text{H}\) NMR measurements were achieved utilizing a phase coherent spin echo pulse spectrometer in magnetic fields of \(H = 0.22-3 \text{ T}\).

3. Magnetization Results and discussion
Open circles in Fig. 2 (a) show the temperature dependence of the magnetization, \(M\), divided by the magnetic field, \(H\), at \(H = 1 \text{ T}\) measured by using a SQUID magnetometer down to 1.9 K. The \(M/H\) obeys the Curie-Weiss law with a Weiss temperature of \(\sim 1 \text{ K}\) above 30 K and shows a Bonner-Fisher-like peak around 3 K. The observed behavior is in a good agreement with the one reported previously [7]. Temperature dependence of \(M/H\) at \(H = 1 \text{ T}\) below 1.9 K is estimated from \(^1\text{H}\) NMR line width [9] and from DC magnetization measurements shown by open triangles and closed circles, respectively. \(M/H\) shows a local minimum around 1 K and levels off at low temperatures, which is
consistent with a gapless ground state of the system in agreement with specific heat measurements [10].

Fig. 2(b) shows the magnetization curve at \( T = 0.09, 0.3, 0.5 \) and 1.8 K. The magnetization has a small fraction which shows Brillouin function-like behavior in the low magnetic field region at low temperatures. This is attributed to spin contribution due to magnetic impurities or open end effects of spin triangle chains by defects. The fraction of the excess magnetization is estimated to be \( \sim 2\% \) of the total magnetization. The most important finding in our DC magnetization measurement is an obvious change in slope of the magnetization curves around 5 T below and above 0.5 K, which can be also seen in change of \( dM/dH \) as shown in the inset. This signature can be attributed to so-called 1/3 plateau in magnetization, since the magnetization around 5 T is \( \sim 1 \mu_B/\text{mol} \), which is one-third of an expected total magnetization of 3 \( \mu_B/\text{mol} \) and 5 T is close to one-third of the saturation magnetic field of 14 T [8].

A phase diagram for a twisted spin tube as a function of \( J_2/J_1 \) and of magnetic field, \( H \), has been proposed theoretically by Fouet et al.[4], using a density matrix renormalisation group calculation. When \( J_2/J_1 \) is smaller than 1.22, the system has a gapped ground state with a two-fold-degenerate state, due to spin chirality. On the other hand, if \( J_2/J_1 \) is large enough, the system is considered an effective \( S=3/2 \) chain with a gapless ground state. The phase transition between the gapped and gapless states takes place for a critical point at \( J_2/J_1 \sim 1.22 \). The 1/3 plateau in the magnetization curve is proposed below \( J_2/J_1 \sim 1.6 \). Although the ratio, \( J_2/J_1 \), is reported previously to be \( \sim 2.16 \) from the temperature-dependence of magnetic susceptibility, our finding of the 1/3 plateau with the gapless ground state indicates that the ratio should fall in the interval \( 1.22 < J_2/J_1 < 1.6 \), suggesting that the Cu-spin tube locates close to the critical point for the phase transition.

4. Proton spin lattice relaxation rate \( 1/T_1 \)

To investigate the dynamical properties of the Cu\(^{2+} \) spins, we completed proton \( T_1 \) measurements in a wide temperature range of \( T = 0.05-100 \) K. Figure 3(a) shows temperature-dependence of \( 1/T_1 \) under various magnetic fields. With decreasing temperature, \( 1/T_1 \) decreases gradually and starts to increase
around 2 K, then shows a peak around 0.6 K. As the external magnetic field increases, the peak temperature of $1/T_1$ shifts to higher temperatures and at the same time the height of $1/T_1$ becomes smaller.

In general, $1/T_1$ is expressed by the Fourier transform of the time correlation function of the transverse fluctuating local field at nuclear sites as [11]

$$
\frac{1}{T_1} = \frac{1}{2} \gamma_N^2 \int \langle h_i(t) h_i(0) \rangle e^{i \omega t} dt ,
$$

(1)

where $\gamma_N$ the nuclear gyromagnetic ratio and $\omega$ the Larmor frequency. When the time correlation function is assumed to decay as $\exp(-\Gamma t)$, the $1/T_1$ can be written as [12]

$$
\frac{1}{T_1} = A \chi T \frac{\Gamma}{\Gamma^2 + \omega^2} ,
$$

(2)

where $A$ is a parameter related to the hyperfine field and $\Gamma$ corresponds to the inverse of the correlation time of the fluctuating hyperfine fields at proton sites due to the Cu$^{2+}$ spins. If $\Gamma$ is independent of temperature, the temperature-dependence of $1/T_1$ is simply expressed by $\chi T$. The open triangles in Fig. 3(a) show $T$-dependence of $\chi T$ estimated from the $T$-dependence of NMR line width. As can be seen in Fig. 3(a), the $T$-dependence of $1/T_1$ scales with that of $\chi T$ above 2 K. The magnetic field-dependence of $1/T_1$ in the region originates from the one-dimensional diffusive nature of spin correlation function, characterized by a $H^{-1/2}$ dependence of $1/T_1$ [13,14]. Thus, nuclear spin relaxation above $\sim$ 2 K is explained by the paramagnetic fluctuations of the Cu$^{2+}$ spins and its fluctuation frequency $\Gamma$ is independent of temperature.

FIG 3. (a) Temperature-dependence of $1/T_1$ at various magnetic fields. Temperature-dependence of $\chi T$ (at $H = 1$ T) estimated from NMR line width is plotted by open triangles. (b) Temperature-dependence of $1/T_1 \chi T$. Solid lines are calculated results of a model described in the text.
Below 2K, the simple paramagnetic fluctuations model cannot reproduce the experimental results. To analyze the T- and H-dependencies of 1/T_1 at low temperatures by using Eq. (2), it is useful to re-plot the data by changing the vertical axis from 1/T_1 to 1/T_1Γ as shown in Fig. 3(b), where the χ_T values are from NMR line width data. According to Eq. (2), 1/T_1Γ is proportional to 1/Γ when Γ >> ω_L (fast-motion regime), while 1/T_1Γ is proportional to 1/Γω_L^2 in the case of Γ << ω_L (slow-motion regime). When Γ = ω_L, 1/T_1Γ shows a peak. Assuming A = 1.96 × 10^12 (rad^2 · K · emu/mol/s^2) and Γ = 3.48 × 10^9 rad/s (rad/s), the experimental results are well reproduced by Eq. (2), as shown in Fig. 3(b) by solid lines for different magnetic fields. These results indicate that the slow-motion regime, whereby the fluctuation frequency of Cu^2+ spins below the peak temperature is less than the NMR frequency range which is of the order of MHz.

For a S = 1/2 one-dimensional quantum spin system with a gapless ground state, 1/T_1 shows temperature-independent behavior at high temperatures and logarithmic increase at low temperatures without any crossover between fast-motion regime and slow-motion regime [15,16]. In the Tomonaga-Luttinger liquid state, 1/T_1 is expected to be proportional to 1/T_0.5 [17]. These predictions are in sharp contrast with the present experimental results. On the other hand, similar slow spin dynamics are observed in some spin frustrated systems, such as the two-dimensional spin frustrated system NiGa_2S_4 [18] and in molecular magnets such as the spin ball Fe30 molecule [19]. Although the origin of slow spin dynamics in the current system is not clear at the present time, this unusual behavior could originate from spin chirality effects due to spin frustrations.

5. Conclusions
We have investigated the magnetic properties of [CuCl_2(tachH)_3]Cl_2, a Heisenberg triangular spin chain, by means of magnetic susceptibility (T = 1.8-300 K), DC magnetization (T = 0.09-1.8 K), and proton NMR (T = 0.05-300 K). The observation of 1/3 plateau in the magnetization curve below 0.5K suggests that the exchange coupling constant ratio J_2/J_1 should be in the range 1.22 < J_2/J_1 < 1.6, and thus that the Cu spin tube locates close to the critical point for the phase transition. T and H-dependences of 1/H-T_1 indicate that Cu spin fluctuations slow down at low temperature to a frequency range less than MHz.

Acknowledgments
The present work was in part supported by Grant-in-Aid for Scientific Researches (A) (No. 2024405) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. One of the authors (H.N.) has been supported by GCOE program: Material Integration. Ames Laboratory is operated for U.S. Department of Energy by Iowa State University under Contract No. DE-AC02-07CH11358. This work at Ames Laboratory was supported by the Office of Basic Energy Science. The work in Pavia was supported by NOE-MAGMAGNET.

References
[1] For example, Frustrated Spin Systems, edited by Diep H T, World Scientific, Singapore, 2005.
[2] Kawamura H 1998 J. Phys.: Condensed Matter 10 4707
[3] Sato M, and Sakai T 2007 Phys. Rev B 75 014411
[4] Fouet J-B, Läuchli A, Pilgram S, Noack R M, and Mila F 2005 Phys. Rev. B 73 014409
[5] Okunishi K, Yoshikawa S, Sakai T, and Miyashita S 2005 Prog. Theo. Phys. Supp. 159 297
[6] Sakai T, Sato M, Okunishi K, Otsuka Y, Okamoto K, and Itoi C 2008 Phys. Rev. B 78 184415
[7] Seeber G, Kögerler P, Karuki B M, and Cronin L 2004 Chem. Commun. 1580
[8] Schnack J, Nojiri H, Kögerler P, Cooper G T J, and Cronin L, 2004 Phys. Rev. B 70 174420
[9] Furukawa Y, Sumida Y, Kumagai K, Nojiri H, Kögerler P, and Cronin L 2009 J. Phys. Conf. Ser. 150 042036
[10] Ivanov N B, Schnack J, Schnalle R, Richter J, Kögerler P, Newton G N, Cronin L, Oshima Y, and Nojiri H 2010 Phys. Rev. Lett. 105 037206
[11] Abragam A, *The Principle of Nuclear Magnetism* (Clarendon Press, Oxford, 1961)
[12] Baek S H, Luban M, Lascialfari A, Micotti E, Furukawa Y, Borsa F, Slageren J van, and Cornia A 2004 *Phys. Rev. B* 70 134434
[13] Borsa F, and Mali M 1974 *Phys. Rev. B* 9 2215
[14] Details of analysis of H dependence of 1/T\textsubscript{1} will be published elsewhere.
[15] Sachdev S 1983 *Phys. Rev. B* 50 13
[16] Takigawa M, Motoyama N, Eisaki H, and Uchida S 1996 *Phys. Rev. Lett.* 76 4612
[17] Goto T, Ishikawa T, Shimaoka Y, and Fujii Y 2006 *Phys. Rev. B* 73 214406 and references therein
[18] Takeya H, Ishida K, Kitagawa K, Ihara Y, Onuma K, Maeno Y, Nambu Y, Nakatsuji S, MacLaughlin D E, Koda A, and Kadono R 2008 *Phys. Rev. B* 77 054429
[19] Schröder C, Fang X, Furukawa Y, Luban M, Prozorov R, Borsa F, and Kumagai K 2010 *J. Phys : Condensed Matter* 22 216007