NMR and μ-SR study on competing Heisenberg chain $Cs_2Cu_2Mo_3O_{12}$

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Abstract. S = 1/2 quasi one dimensional Heisenberg chain $Cs_2Cu_2Mo_3O_{12}$ has two dominant exchange interactions of the nearest-neighbouring ferromagnetic $J_1 = -93$ K and the second nearest-neighbouring antiferromagnetic $J_2 = +33$ K. These competing interactions on the spin chain are expected to bring rich physics, such as frustration or nematic Tomonaga-Luttinger liquid (TL) phase. In order to investigate its ground state at zero and finite fields, we have performed ^{133}Cs-NMR experiments under the wide range of magnetic field up to 14 T, and μ-SR at zero field. In low-field region, the existence of long range magnetic order was demonstrated below 2 K. In the higher field region between 7 T and the saturation field $H_s = 9.15$ T, no evidence for magnetic order was confirmed at finite temperatures.

1. Introduction

The ground state of S = 1/2 Heisenberg spin chain is the Tomonaga-Luttinger liquid (TLL) state, where the spatial spin correlation obeys the power law. This is a critical state, and the system may undergo a phase transition at a finite temperature with aid of a tiny inter-chain interaction. We focus attention on the quasi-one dimensional spin chain $Cs_2Cu_2Mo_3O_{12}$ [1], which is isomorphic to $Rb_2Cu_2Mo_3O_{12}$ [2], and is reported to be described by the J_1- J_2 model with two dominant exchange interactions of the nearest-neighboring ferromagnetic $J_1 = -93$ K and the second nearest-neighboring antiferromagnetic $J_2 = +33$ K [2]. In this competing chain model, the existence of nematic TLL state is theoretically proposed under high field region near the saturation [4-8]. The ground state of $Cs_2Cu_2Mo_3O_{12}$ under zero or finite field is still not clear until now. The uniform susceptibility approaches a finite value at zero temperature without showing an anomaly[1], suggesting a gapless ground state. Quite recently, preliminary results on NMR[9] and specific heat[12] have reported the existence of magnetic order at low temperatures below 2 K under a finite field of 5 T and zero field respectively. In order elucidate microscopically its ground state in a wide range of magnetic field, we have performed μSR and NMR study in fields up to 14 T. In this article we show the field dependence of magnetic order critical temperature, and also the temperature dependence of NMR longitudinal nuclear spin relaxation rate $1/T_1$ in paramagnetic state, which shows a drastic change with applied magnetic field.

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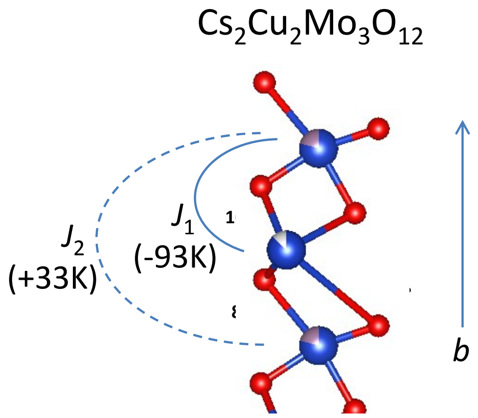

Figure 1. Schematic drawing of the ribbon-chain structure consisting of Cu (blue sphere) and Oxygen (red smaller sphere). Exchange paths of $\boldsymbol{J_1}$ and $\boldsymbol{J_2}$ are shown by curves [1].

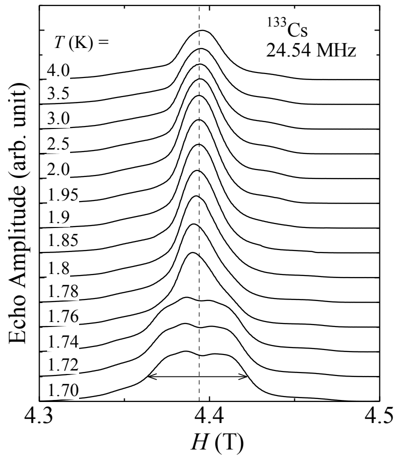

Figure 2. Typical profiles of ^{133}Cs-NMR spectra for powder sample at various temperatures. The horizontal arrow indicates the definition of resonance line width.

2. Experimental

The powder sample of $Cs_2Cu_2Mo_3O_{12}$ was obtained by the conventional solid-state reaction method[1]. Its crystal structure belongs to the space group of $C2/c$ and consists of zigzag chains or so-called ribbon chains [1,3], which run along b-axis (Fig. 1) and of intervening ions of Mo and Cs located at interstitial site between chains, maintaining the good one-dimensionality. The NMR-nucleus Cs has the three inequivalent sites of 4*d*, 4*e* and 8*f*, and the distances between Cs and Cu atoms are between 4 and 6 Å, from which a moderate hyperfine coupling is expected.

NMR measurements were performed in the field region between 1.5 and 14 T and in the temperatures down to 0.3 K. Spectra were obtained by recording the spin-echo amplitude against magnetic field, which was ramped slowly around the zero-shift position [13]. For the sample was powder, both the *eqQ*-splitting of ^{133}Cs ($I = 7/2$) and the signal from inequivalent sites are smeared out, so that only a single broad peak was observed in the paramagnetic temperature region.

The longitudinal spin relaxation rate $1/T_1$ was obtained by the conventional saturation-recovery method with a pulse-train for saturation. We note here that due to an extraordinary long T_2, the transverse nuclear spin relaxation time, the distance between each pulse within the train must be set apart by as long as 100-200 μsec. After the saturation, the nuclear spin polarization was traced until its difference from the thermal equilibrium value reached one percent. Obtained relaxation curves were fitted to the stretched exponential function $1 - e^{-(\tau/T_1)^\beta}$, where β is a temperature dependent constant, and its difference from unity reflects microscopic inhomogeneity in the system[9-11]. The effect of quadrupole splitting [15] was observed neither in relaxation nor spectrum experiments, which is considered to be due to the extremely small electric quadrupole moment of ^{133}Cs nuclei. The constant β was nearly temperature independent around 0.5 above 2 K, and was decreased gradually to 0.2 below 2 K [9,14]. The origin of its temperature dependence is not determined at this stage, though it is speculated to be related to microscopic inhomogeneity[10] in this system.

The zero-field (ZF) μSR experiment was performed at RIKEN-RAL muon facility in ISIS, UK. In this experiment, the spin-polarized muon bunch with a momentum of 27 MeV/c is injected into the sample and the time-evolution of muon spin polarization was traced until $\tau = 8$ μsec. The obtained depolarization curves were analyzed with the function $G_{\rm KT}(\tau;\sigma)e^{-\lambda\tau}$, where $G_{\rm KT}$ is Kubo-Toyabe function, σ, the quasi-static field distribution contributed from nuclear moments and λ, the

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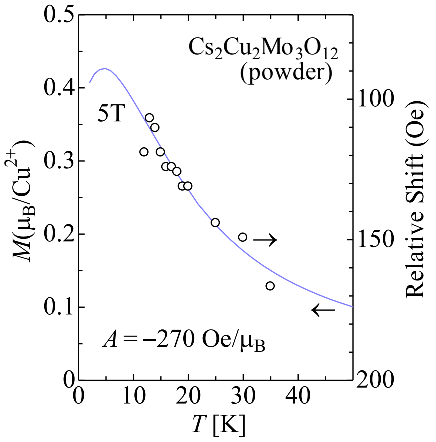

Figure 3. Scaled plot of the temperature dependences of NMR shift and uniform magnetization to obtain the effective hyperfine coupling constant $\boldsymbol{A}$.

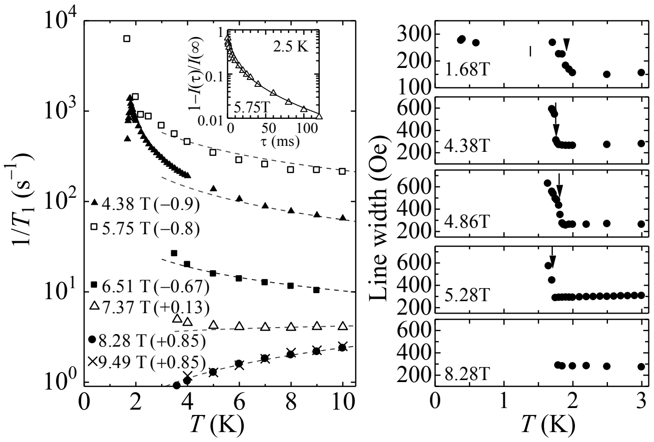

Figure 4. (Left) Temperature dependence of the T_1^{-1} in various fields. Dashed curves show the power law $T^{2\mathrm{K}-1}$; the values of $2K-1$ are shown with the field values. The inset show typical relaxation curves. (Right) The line width taken at various applied fields. T_N defined as an abrupt increase in the width is shown by vertical arrows.

depolarization rate due to the dynamical spin fluctuation[11,14,16]. In the present experiments, σ ≃0.068 $\mu\mathrm{sec}^{-1}$ was found to be temperature independent, and the information of spin state was obtained solely from the temperature dependence of λ.

3. Results and Discussion

Figure 2 shows a typical profile of spectra at various temperatures. With decreasing temperature, the line width slightly decreased below 10 K, reflecting the decrease in uniform susceptibility [1,12], and abruptly increased again below 1.85 K. Figure 3 shows the temperature dependence of the uniform susceptibility and the resonance line shift in the paramagnetic state. By scaling those two quantities, we obtained the effective hyperfine coupling constant $A = -270\,\mathrm{Oe}/\mu_\mathrm{B}$, which is large enough to detect the magnetism in copper site by NMR. Note that this value of A includes the contributions both from the isotropic and anisotropic parts, because the definition of shift is the peak top rather than the mass center of peak.

Next, we show the temperature dependences of $1/T_1$ and the line width in Fig. 4. At the field 4.38 T, a critical divergence in $1/T_1$ [17] and an abrupt increase in the line width took place at the same temperature 1.8 K. This clearly demonstrates the existence of long range magnetic order, which is consistent with our previous report [9]. This finite T_N in the quasi-one dimensional system is considered to be brought by a weak inter chain interaction. Thus, we can safely assign the increase in the line width at 1.68 and 5.28 T to the magnetic order. At the higher field of 5.75 T, $1/T_1$ showed a clear diverging toward 1.7 K, and we can judge that T_N must be located in its vicinity, that is, slightly below 1.7 K, though we have observed no increase in the line width down to 1.7 K.

At field 8.28 T, $1/T_1$ monotonically decreased with decreasing temperature without showing any sign of the critical divergence. The line width did not show any abrupt increase down to 1.7 K. These indicate an absence of magnetic order at finite temperatures at this and the higher fields. The data at 7.37 and 6.51 T are, however, critical, because $1/T_1$'s stayed nearly constant, and no broadening was observed (not shown) down to 1.7 K. We can therefore only say that a possible T_N for these two field points may exist between 1.5 and 0 K.

Zero field μ-SR (ZF) data in Fig. 5 shows that the muon spin depolarization rate λ abruptly increased below $T_\mathrm{N} = 1.85$ K. This anomaly coincides with the recent report on the specific heat by

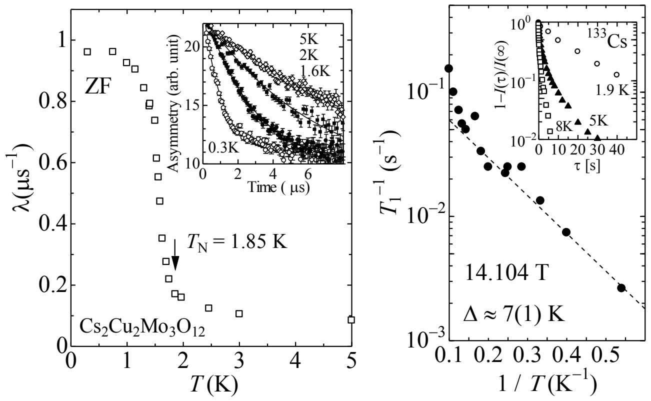

Figure 5. (Left) Temperature dependence of μ-SR depolarization rate at zero field. $\boldsymbol{T_N}$ is shown by an arrow. The inset shows typical depolarization curves. (Right) Temperature dependence of $\boldsymbol{T_1^{-1}}$ at high field in the saturated region.

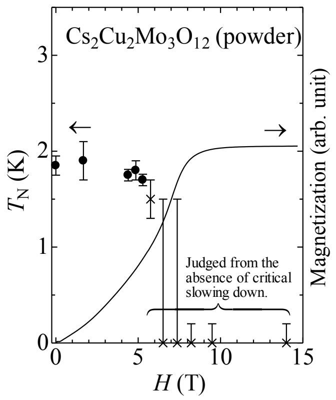

Figure 6. Field dependence of magnetization and T_N, estimated by NMR line width and T_1^{-1}.

Fujimura *et al.* [12], and hence confirms microscopically the existence of long range magnetic order at zero field. In general, however, the dynamical spin fluctuation contributes to λ through its fluctuation amplitude δH and its characteristic frequency ω_C as $\delta H^2/\omega_C$ [16]. So, our observation only assures an increase in δH and/or a slowdown in ω_C. We can assign it to the evidence of magnetic order under zero-field, because it agreed with the result of specific heat [12], and also with extrapolation of T_N under finite fields.

We combine all T_N's determined under various fields and plot them onto *H*-*T* diagram in Fig. 6. As increasing, field from zero, one can see that T_N stays nearly constant until 5 T, from which it decreases steeply to zero at around 6 T, which is significantly lower than the saturation field $H_s = 9.15$ T [12]. In many cases of gapped quantum spin systems so far reported [19,20], a field-induced magnetic order takes place at finite temperature within a magnetization slope region, that is, the field at which T_N becomes zero must coincide with H_s. The discrepancy found in this system suggests the relevancy with the spin nematic state under high fields [4-8]. However, in order to judge it, more detailed data are necessary, and furthermore, preparation of a single crystal is also required to avoid an ambiguity in the determination of H_S.

At the highest measured field 14.1 T, $1/T_1$ showed the thermal-activation type temperature dependence (Fig. 5), indicating opening of an energy gap in the spin-excitation spectrum. Adapting the value of saturation field $H_S = 9.15$ T [12], we compared the obtained gap $\Delta \simeq 7(1)$ K with the Zeeman energy $g½\mu_B(14.1 - H_s)$ to find that $g \simeq 4$. This anomalous value suggests a coherent flip of each neighboring two spins in the saturated field region [21], reflecting the ferromagnetic interaction between neighboring two spins.

Finally, we refer the temperature dependence of $1/T_1$ in the paramagnetic state. As shown in Fig. 4 (left), $1/T_1$'s for the entire field range below H_s obey the power law above 5 K, which is shown by dashed curves. The power index shows significant dependence on the applied field. In the TLL state, the spatial spin correlation function obeys the power law as x^{-2K}, where the field-dependent constant K is Luttinger parameter. The longitudinal and transverse components of spin fluctuation contribute to $1/T_1$ through the anisotropic hyperfine interaction, and let it exhibit the power law temperature dependence of T^{2K-1} and $T^{1/2K-1}$, respectively [22-24]. In nematic or multipolar TLL state, where the transverse component is strongly suppressed at low temperatures [18,25], the term T^{2K-1} solely dominates the temperature dependence of $1/T_1$. This means that $1/T_1$ may decrease at low temperatures when $K > ½$. Note that in the ordinary TL liquid state [26,27], $1/T_1$ must always increase at low temperatures except for the singular point $K = ½$. The observed behavior of $1/T_1$, that is, $2K-1$ monotonically increases with increasing field as shown in Fig. 4 (left), seems to be well described above scenario. However, one must be very careful about the fact that $1/T_1$ generally decreases at low temperature in the saturation region, reflecting an opening of spin excitation gap. In order to conclude that the observed behavior is due to the characteristic spin fluctuation in the nematic TLL, determination of the hyperfine coupling tensor is indispensable, which are in the progress.

Summary

NMR and ZF μ-SR experiments on the $S = ½$ Heisenberg competing spin chain system $Cs_2Cu_2Mo_3O_{12}$ were performed in the wide-field range from zero to 14 T. The existence of long range magnetic order under the fields below 6 T was demonstrated by the broadening in NMR resonance line, critical divergence of $1/T_1$, or abrupt increase in μ-SR depolarization rate. $T_N \simeq 1.8$ K was nearly field independent until 6 T, above which $1/T_1$ decreased with decreasing temperature, indicating no magnetic order .

Acknowledgement

This work was partly supported by JSPS KAKENHI Grant Number 26108713, 15K05148 and. It was also supported by the Sophia University Special Grant for Academic Research. A part of the experiments was performed at High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.

References

[1] M. Hase *et al.,* J. Appl. Phys. 97 (2005) 10B303.
[2] M. Hase *et al.,* Phys. Rev. B70 (2004) 104426.
[3] S. F. Solodovnikov et al.: J. Struc. Chem. 38 (1997) 765.
[4] M. E. Zhitomirsky et al.: Euro Phys. Lett. 92 (2010) 37001.
[5] M. Hagiwara et al.: J. Phys. Conf. Ser. 320 (2011) 012049.
[6] H. Tsunetsugu et al.: J. Phys. Soc. Jap. 75 (2006) 083701.
[7] Lars Kecke et al.: Phys. Rev. B76, 060407R (2007).
[8] T. Hikihara et al.: Phys. Rev. B78 (2008) 144404.
[9] Y. Hoshino *et al.,* JPS Conf. Proc. 3 (2014) 014012.
[10] M. Urano *et al.*, Phys. Rev. B76 (2007) 024505.
[11] T. Suzuki et al.: J. Phys. Soc. Jpn. 76 (2007) 074704.
[12] A. Fujimura *et al.,* IEEE Transactions on Magnetics 99 (2016), *in press*.
[13] H. Inoue *et al. ,* Phys. Rev. B79 (2009) 174418.
[14] T. Suzuki et al.: Phys. Rev. B79 (2009) 104409.
[15] S. Mishima et al.: J. Appl. Phys. 87 (2000) 5134.
[16] S. Nakajima *et al.,* J. Phys. Soc. Jpn. 81 (2012) 063706.
[17] K. Kanada *et al.*, J. Phys. Soc. Jpn. 76 (2007) 064706.
[18] M. Sato et al.: Phys. Rev. Lett. 110, 077206 (2013).
[19] G. Chaboussant et al.: Phys. Rev. Lett. 80 (1998) 2713.
[20] M. Jaime et al.: Phys. Rev. Lett. 93 (2004) 087203.
[21] N. Büttgen *et al.*: Phys. Rev. B90 (2014) 134401.
[22] T. Sakai, J. Phys. Soc. Jpn. 64 (1995) 251.
[23] T. Suzuki *et al.*: Phys. Rev. B 74 (2006) 172410.
[24] T. Suzuki *et al.*: Phys. Rev. B70 (2004) 054419.
[25] M. Sato et al. Phys. Rev. B83 (2011) 064405.
[26] M. Klanšjek et al.: Phys. Rev. Lett. 101 (2008) 13727.
[27] K. Ninios et al.: Phys. Rev. Lett. 108 (2012) 097201.