Critical Slowing Down of Triangular Lattice Spin-3/2 Heisenberg Antiferromagnet Li$_7$RuO$_6$ via $^7$Li NMR

YUTAKA ITOH$^1$, CHISHIRO MICHIOKA$^1$, KAZUYOSHI YOSHIMURA$^1$, KANAKO NAKAJIMA$^2$, and HIROHIKO SATO$^2$

$^1$Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502
$^2$Department of Physics, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551

We report $^7$Li NMR studies of single crystals of triangular-lattice Heisenberg antiferromagnet Li$_7$RuO$_6$. Slow critical divergence with a wide critical region of $|T/T_N - 1| \leq 7$ was observed in $^7$Li nuclear spin-lattice relaxation rate. The slowing down of staggered spin fluctuations was analyzed in a renormalized classical region of a two-dimensional triangular-lattice non-linear sigma model. A spin stiffness constant was found to reduce to about 20 % from the value in a spin-wave approximation. The effect of spin frustration, e.g., $Z_2$ vortex excitations on the critical phenomena is suggested.

KEYWORDS: Li$_7$RuO$_6$, triangular lattice, spin frustration, NMR, renormalized classical region

Spin frustration effect of a triangular lattice Heisenberg antiferromagnet has been one of the central issues in physics and chemistry of magnetic insulators. The ground state is classically a long range ordering state with the 120° spin structure, but the quantum mechanical ground state might be a gapped or gapless quantum spin liquid. Non-linear sigma model and field theoretical treatments turned out to be the relevant model and to give us powerful methods to describe the low energy excitations. They were also applied to the actual critical phenomena of triangular spin systems.

A delafossite-type Li$_7$RuO$_6$ has been at first reported as hexagonal “Li$_{8-\delta}$RuO$_6$.” However, a detailed analysis on powder and on single crystal revealed that the actual composition is “Li$_7$RuO$_6$” and the structure is slightly distorted from an ideal hexagonal lattice. Li$_7$RuO$_6$ is triclinic and has the superlattice structure of the Li deficiency in the double Li layers. Figures 1(a) and 1(b) show the crystal structure and the triangular lattice, respectively. Single Li$_2$RuO$_6$ layer and double Li layers are stacked with each other. The Li$_2$RuO$_6$ layer consists of a triangular lattice of RuO$_6$ octahedrons and a Li honeycomb lattice. The Li ions occupy 12 sites in the RuO$_6$ layer and 30 sites in the Li deficient layers in unit cell, which are crystallographically inequivalent. For

Fig. 1. (a) Schematics of crystal structure of Li$_7$RuO$_6$ and (b) the top view of a triangular lattice Ru plane. (c) Inverse magnetic susceptibility $\chi^{-1}$ and (d) the magnetic susceptibility $\chi$ of a single crystal Li$_7$RuO$_6$. The solid lines are the best fits by an inverse Curie-Weiss law. The arrow indicates $T_N \approx 6.5$ K.
a hexagonal model of Li₆RuO₆, the staggered magnetic field from Ru would be cancelled out at the Ru-plane Li site. However, for the actual Li₇RuO₆, since the Li ions occupy non-ideal positions deviated from the center of the Ru triangle, then the 120° staggered spin fluctuations can be probed through the Li NMR. Li₇RuO₆ is a deformed triangular lattice system. The detail of the crystal growth and the structure analysis will be published in a separated paper.²⁰

Uniform magnetic susceptibility χₐ (α = || and ⊥ denote H || plane and H ⊥ plane) shows a slightly anisotropic Curie-Weiss behavior χ = C/(T − Θ) with C = 1.89 emu/mol-Ru and Θ = −73 K at high temperatures. Figures 1(c) and 1(d) show the inverse magnetic susceptibility χ⁻¹ up to 300 K and the magnetic susceptibility χ on an enlarged scale for a single crystal, respectively. Upon cooling, χₐ makes a maximum at about 12.5 K and drops sharply at the Neel temperature TN ≈ 6.5 K.¹⁹,²⁰ The broad maximum behavior indicates a low dimensional magnet. The Curie constant C is close to the value for S = 3/2 and g = 2. For a Heisenberg spin Hamiltonian ΣJₙᵣSᵣ · Sᵣ with the z nearest-neighbor exchange interaction Jₙᵣ between Ru ions, the Weiss temperature Θ is given by

Θ = S(S + 1)zJₙᵣ, (1)

in the mean field approximation. Using S = 3/2 (Ru⁵⁺) and z = 6, we estimated the superexchange interaction Jₙᵣ = −9.7 K. Since TN ≈ 6.5 K and Θ = −73 K, we obtain the ratio of TN/Θ ≈ 0.089, which is nearly the same as 0.082 for VCl₂ with S = 3/2 (V⁴⁺).²¹ These are the low dimensional characteristics of (i) and (ii). Thus, the layered compound Li₇RuO₆ is a quasi-two dimensional antiferromagnet.

In this Letter, we report ⁷Li NMR studies of single crystals of triangular-lattice Heisenberg antiferromagnet Li₇RuO₆. We found slow critical divergence with a wide critical region of [T/Tₐ − 1] ≤ 7 in ⁷Li nuclear spin-lattice relaxation rate, which is due to the slowing down of staggered spin fluctuations. From the analysis by renormalized classical fluctuations, we found the reduction of a spin stiffness constant, possibly due to the spin frustration effect.

Single crystals of Li₇RuO₆ were grown from the mixture of RuO₂ and a large amount of LiCO₃ flux heated in an oxygen atmosphere at 950 °C. Typically 0.5×0.5×0.01 mm sized and plate-like single crystals were obtained.²⁰

The plane and the vertical axes are confirmed to be the ab plane and the c axis of the quasi-hexagonal lattice, respectively. X-ray diffraction patterns for the powdered samples indicated the samples in a single phase. We performed ⁷Li (nuclear spin I = 3/2 and nuclear gyromagnetic ratio γₙ/2π = 16.546 MHz/T) NMR spin-echo measurements at H = 7.48414 T for the samples in which the several single crystal pieces were put on a plate. The NMR frequency spectra were obtained from Fourier-transformed spin-echoes or summing them at several frequencies and frequency-swept spin-echo intensity. The ⁷Li nuclear spin-lattice relaxation curves were measured by an inversion recovery technique and the relaxation times T₁'s were obtained from the fits by a stretched exponential function of exp{−(t/T₁)β} (t is the time after the inversion pulse).

Figure 2(a) shows ⁷Li NMR frequency spectra of the single crystals of Li₇RuO₆ at H ⊥ plane (solid curves and closed circles) and at H || plane (open circles). The vertical line at 123.8343 MHz indicates the ⁷Li NMR spectrum peak of LiCl₄ for a reference of zero shift. The inset shows the best fits by three Gaussian functions. (b) Knight shift ⁷K plotted against the bulk magnetic susceptibility χₐ with temperature as an implicit parameter.

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Fig. 3. (a) Temperature dependences of ⁷Li nuclear spin-lattice relaxation rates 1/T₁ of S₁ (closed circles) and S₂ (open triangles) at H ⊥ plane and T > Tₐ. The inset figure shows semi-log plots of the temperature dependences of the stretched exponents β. (b) Log-log plots of ⁷Li nuclear spin-lattice relaxation rates 1/T₁ at H ⊥ plane against the reduced temperature (T−Tₐ)/Tₐ.

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$T > 200$ K, a single sharp $^7$Li NMR spectrum and no quadrupole splits were observed. Upon cooling, the NMR spectrum shifts to higher frequency side and a weak signal separates and shifts more largely. At $4.2$ K, both NMR spectra at $H \perp$ plane and $H \parallel$ plane are broadened nearly symmetrically. The featureless symmetric broadening below $T_N$ indicates the emergence of internal magnetic field of an incommensurate staggered moments along the $ab$ plane and the $c$ axis.

The inset shows three Gaussian functions fit to the NMR spectrum at $H \perp$ plane and $T = 19.8$ K. A sharp strong peak and a broad higher frequency peak are denoted by S1 and S2, respectively. S3 just adjusts the foot of the spectrum, whose Knight shift is $\sim 100$ ppm and nearly independent of temperature. From the NMR intensity, the strong peak S1 and weak S2 can be assigned to the Li sites in the double Li layers and in the RuO$_6$ triangle lattice layer, respectively. The assignment at $H \parallel$ plane at $T > T_N$ not shown in Fig. 2(a) was less clear, since at least 4 peaks were observed. The lowest and highest frequency peaks are assigned to S1 and S2, respectively.

Figure 2(b) shows $^7$Li Knight shifts of S1 and S2 plotted against the bulk magnetic susceptibility $\chi$ with temperature as an implicit parameter. The bulk magnetic susceptibility $\chi$ is expressed by $\chi_{\text{B}}$ and $A$ and 2 denote $S_1$ and $S_2$, respectively. The positive $\chi$ at $T > T_N$ plane at $T > T_N$ shows the divergence behavior due to the critical slowing down was estimated.

In general, the high temperature limit of $1/T_1$ in the exchange narrowing is expressed by

$$
\frac{1}{T_{1\infty}} = \sqrt{\frac{\pi}{2}} \frac{S(S+1)}{3} \frac{2a_t^2 A_{\text{ex}}^2}{\omega_{\text{ex}}^2} \quad \text{(2)}
$$

and

$$
\omega_{\text{ex}}^2 = \frac{2}{3} z S(S+1) \left( \frac{k_B T_{\text{nn}}}{k_B} \right)^2. \quad \text{(3)}
$$

The hyperfine field at the in-plane Li results from the 3 nearest neighbor Ru spins. The number of the nearest neighbor exchange coupled Ru spins is 6. Putting $z = 6$, $S = 3/2$, $A_{\text{ex}}(2) = 2.0 \text{ kOe}/\mu_B$ and $J_{\text{nn}} = -9.7$ K for eqs. (2) and (3), we obtain $1/T_{1\infty} = 340 \text{ s}^{-1}$, which is the same order of magnitude but slightly smaller than the actual $1/T_1 \approx 400$ and $600 \text{ s}^{-1}$ for S1 and S2 above $200$ K, respectively. The experimental value of $T_1$ depends on the fitting function more or less. Using the fitting function of a double exponential function, we obtained a long component of $1/T_1 \approx 277$ and $433 \text{ s}^{-1}$ for S1 and S2, respectively, being the same order of magnitude of the estimated $1/T_{1\infty}$.

Figure 3(b) shows log-log plots of $7(1/T_1)$ against the reduced temperature $(T - T_N)/T_N$. The critical divergence of $1/T_1$ starts from $|T/T_N - 1| \sim 7$. Although such a wide critical region is not usually regarded as a three dimensional critical region, we tried to apply a power law of $|T/N/(T_N - T_N)|^n$ and then obtained $n = 0.45$. This is close to the mean field value.

Figure 4 shows log-log plots of magnetic field of an incommensurate staggered moments along the $ab$ axis. The inset figure shows semi-log graphs of the temperature dependences of the stretched exponents $\beta$. At high temperatures, $1/T_1$ levels off, which indicates the exchange narrowing limit. At low temperatures, $1/T_1$ shows the divergence behavior due to the critical slowing down of the staggered spin fluctuations.

![Figure 4](image_url)
the critical phenomenon of Li$_7$RuO$_6$.

For the frustrated quantum antiferromagnets, the nonlinear sigma model description tells us the magnetic correlation length $\xi = \frac{1}{\sqrt{T}} \exp(4\pi \rho_a / T)$

$$\xi \propto \frac{1}{\sqrt{T}} \exp(4\pi \rho_a / T)$$

(4)

with a spin stiffness constant $\rho_a$ ($\alpha = \perp$ and $\parallel$ plane) and the nuclear spin-lattice relaxation rate $1/\tau_{\rho}$.

$$\frac{1}{\tau_{\rho}} \propto T^3 \exp(4\pi \rho_a / T).$$

(5)

The spin stiffness constant $\rho_\perp$ is given by

$$\rho_\perp = \sqrt{3} Z_\perp S^2 |J| \approx 1.51|J|,$$

(6)

where a renormalization factor $Z_\perp$ is estimated by a spin-wave approximation and $1/\sqrt{T}$ expansion. Equations (4) and (5) are applicable to the low temperature states at $T < 2 \pi \rho_a$. For the frustrated quantum antiferromagnets, the non-

Figure 5 shows semi-logarithmic $1/T_1 T^3$ against $10/T$ for Li$_7$RuO$_6$ at $H \perp$ plane. The straight line is the fitting function of eq. (5).

In conclusion, we found slow critical divergence with a wide critical region of $|T/T_N - 1| \leq 7$ in $^6$Li nuclear spin-lattice relaxation rate for the triangular-lattice antiferromagnet Li$_7$RuO$_6$. We applied renormalized classical staggered spin fluctuations to the slow divergence and then obtained the reduction of a spin stiffness constant, suggesting the spin frustration effect.

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