Li NMR Studies of LiCrO$_2$

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(Received September 30, 2013)

We report on $^7$Li NMR studies of a spin $S = 3/2$ triangular lattice antiferromagnet LiCrO$_2$ (Néel temperature $T_N = 62$ K) in the paramagnetic state by using the free-induction decay of $^7$Li nuclear magnetization. We observed critical divergence of the $^7$Li nuclear spin-lattice relaxation rate $1/T_1$ near $T_N$, a narrow critical region, and a critical exponent $\nu = 0.45$ from a fit of $1/T_1 \propto (T/T_N - 1)^{-\nu}$. Although spin frustration effects have been explored for this system, the dynamical critical phenomena suggest that LiCrO$_2$ in the critical region is a poor low dimensional antiferromagnetic system.

**KEYWORDS:** spin frustration effect, NMR, LiCrO$_2$

1. Introduction

LiCrO$_2$ is a quas-two dimensional triangular lattice Heisenberg antiferromagnet with a Néel temperature $T_N \approx 62$ K. The crystal structure is an ordered rock salt structure, where the Cr$^{3+}$ ion carries a local moment of $S = 3/2$ on the triangular lattice. Non Curie-Weiss behavior of the uniform spin susceptibility below about 450 K suggests a low dimensional exchange network and a possible spin frustration effect. The Weiss temperature $\Theta$ is estimated to be -700 K from the Curie-Weiss susceptibility fit above about 450 K [1]. The spin frustration effects on the paramagnetic state and the magnetic ordered state have been explored by using ESR [2], neutron diffraction [3], NMR and thermodynamic properties [4] and muon spin rotation ($\mu$SR) [5]. The temperature dependences of the ESR line width [2] and $^7$Li NMR spin-echo relaxation rate [4] were associated with an exponential increase of thermally excited $Z_2$ vortices (topological defects) [6]. However, three dimensional magnetic structure with double-$Q$ 120° ordering vectors has been observed in the neutron diffraction [3] and $\mu$SR [5]. Two dimensional renormalized classical spin correlation also yields an exponential divergence toward $T = 0$ K in the NMR relaxation rate for a triangular lattice Heisenberg antiferromagnet such as Li$_7$RuO$_6$ [7]. There remains to be solved whether the two dimensional spin correlation predominates in the paramagnetic state of LiCrO$_2$. We have performed a detailed $^7$Li NMR experiment using the free induction decay (FID) of $^7$Li nuclear magnetization for LiCrO$_2$.

In this paper, we report on $^7$Li NMR studies of LiCrO$_2$ polycrystalline samples in the paramagnetic state. We observed critical divergence of the $^7$Li nuclear spin-lattice relaxation rate $1/T_1$ near $T_N$, a narrow critical region, a critical exponent $\nu = 0.45$ by a fit of $1/T_1 \propto (T/T_N - 1)^{-\nu}$, and no regimes of the two dimensional renormalized classical spin correlation.

2. Experiments

Powder samples of LiCrO$_2$ have been synthesized by a conventional solid-state reaction method. Appropriate amounts of Li$_2$CO$_3$ and Cr$_2$O$_3$ were mixed, palteded and fired at 1150°C for 24 hours.

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in air. The products were confirmed to be in a single phase from measurements of the powder X-ray
diffraction patterns. A phase-coherent-type pulsed spectrometer was utilized to perform the $^7$Li NMR
(nuclear spin $I = 3/2$) experiments in an external magnetic field of 1.00 T. The NMR frequency spectra
were obtained from Fourier transformation of the $^7$Li FID signals. $^7$Li nuclear spin-lattice relaxation
curves $^7p(t) = 1 - F(t)/F(\infty)$ (recovery curves) were obtained by using an inversion recovery
technique as a function of time $t$ after an inversion pulse, where FID $F(t)$, $F(\infty)[\equiv F(10T_1)]$ and $t$
were recorded.

3. Results

Figure 1(a) shows the Fourier-transformed (FT) spectra of $^7$Li FID signals in LiCrO$_2$ at 77 and
289 K at a reference frequency of 16.5520 MHz. The NMR line of LiCl$_{aq}$ represents the reference
frequency at zero shift at 1.00 T. No appreciable change is found in the linewidth of the NMR spectra
from 289 K to 77 K. The effects of relocation of the Li ions and the motion, which were suggested
by the $\mu$SR studies [5], could not be found in the NMR spectra of our samples.

Figure 1(b) shows the recovery curves $^7p(t)$ of $^7$Li NMR FID signals as a temperature is de-
creased. The solid lines are the results from the least-squares fit by a single exponential function

$$^7p(t) = p(0)\exp(-t/T_1)$$

where $p(0)$ and the $^7$Li nuclear spin-lattice relaxation time $^7T_1$ are the fit parameters.

Figure 2(a) shows the temperature dependence of $1/T_1$. With cooling down, $1/T_1$ shows a crit-
ical divergence near $T_N$, while it levels off at higher temperatures above about 200 K. The high
temperature value of $1/T_1$ is estimated to be $69 \text{ s}^{-1}$. The paramagnetic state above about 200 K is
in the exchange narrowing limit. Then, the upper limit of an exchange coupling constant $J$ is $\sim 200$
K. The Curie-Weiss spin susceptibility fit at higher temperatures indicates $J = 80 \text{ K}$ [1, 4].

Figure 2(b) shows normalized $(1/T_1)/(1/T_{1\infty})$ versus reduced temperature $[T - T_N]/T_N$. The
solid line is the result from the least-squares fit by $1/T_1 = (C/\sqrt{T_{1\infty}})(T/T_N - 1)^{-w}$ where $C$ and $w$
are the fit parameters. The critical exponent is estimated to be $w = 0.45$. A mean field theory for a three dimensional isotropic Heisenberg antiferromagnet leads to $w = 1/2$ [8]. A dynamic scaling theory indicates $w = 1/3$ for a three dimensional isotropic Heisenberg model [9] and $w = 2/3$ for a three dimensional uniaxial anisotropic Heisenberg model [10]. The exponent of $w = 0.45$ suggests that LiCrO$_2$ in the critical region is described by a three dimensional interaction model.

**Fig. 2.** (a) $1/T_1$ against temperature. $1/T_1$ shows a critical divergence near $T_N$. The dashed line indicates $1/T_1\infty = 69$ s$^{-1}$. (b) Normalized $(1/T_1)/(1/T_1\infty)$ against temperature $|T - T_N|/T_N$. The solid line indicates $1/T_1 = (T/T_N - 1)^{-w}$.

**Fig. 3.** Normalized $(1/T_1)/(1/T_1\infty)$ against reduced temperature $(T - T_N)/T_N$ for three dimensional (CuO [11], FeF$_2$ [12]), triangular-lattice (Li$_7$RuO$_6$ [7], NiGaS$_4$ [13]) and the present LiCrO$_2$. Figure 3 shows log-log plots of the normalized $(1/T_1)/(1/T_1\infty)$ against the reduced temperature $(T - T_N)/T_N$ for three dimensional antiferromagnets (CuO [11], FeF$_2$ [12]), triangular-lattice antiferromagnets (Li$_7$RuO$_6$ [7], NiGaS$_4$ [13]) and the present LiCrO$_2$. The critical divergence of
(1/T_1)/(1/T_1^\infty) of LiCrO_2 coincides with a part of FeF_2, which is a uniaxial anisotropic Heisenberg system. The onset of the increase in the NMR relaxation rate near T_N empirically categorizes the critical region. The region of |T−T_N|/T_N ≤ 10 has been assigned to the renormalized classical regime with the divergent spin-spin correlation length toward T = 0 K [7]. The region of |T−T_N|/T_N ≤ 1.0 has been assigned to the three dimensional critical regime with the divergent spin-spin correlation length toward T_N. Thus, the narrow critical region of |T−T_N|/T_N ≤ 1 also indicates that LiCrO_2 is in the three dimensional critical regime.

4. Discussions

The theoretical analysis of the non-linear sigma model for the spin S frustrated quantum antiferromagnets gives us the magnetic correlation length [14–17]

\[ \xi \propto \frac{1}{\sqrt{T}} \exp\left(\frac{4\pi \rho_s}{T}\right) \]  

(2)

with a spin stiffness constant \( \rho_s \) and the nuclear spin-lattice relaxation rate

\[ \frac{1}{T_1 T_3} \propto \exp\left(\frac{4\pi \rho_s}{T}\right). \]  

(3)

Here, the spin stiffness constant \( \rho_s \) is expressed by

\[ \rho_s = \frac{\sqrt{3}}{2} Z_s S^2 J_s, \]  

(4)

where a renormalization factor \( Z_s \) is calculated by a spin-wave approximation and 1/S expansion and \( J_s \) is the nearest neighbor exchange coupling constant [18].

![Fig. 4. (a) Semi-logarithmic plot of 1/T_1 T^3 against inverse temperature 100/T for LiCrO_2. The dash curve indicates 1/T_1 T^3 = 1/T_1^\infty. The solid curve indicates 1/T_1 T^3 ∝ (T/T_N − 1)^{-w}. (b) Semi-logarithmic plots of 1/T_1 T^3 against inverse temperature 10/T for Li_7 RuO_6 [7] and NiGa_2S_4 [13]. The solid lines indicate 1/T_1 T^3 ∝ \exp(4\pi \rho_s/T).](image-url)
Table 1. Spin stiffness constants and exchange coupling constants estimated from the analysis using the two dimensional renormalized classical model for triangular lattice compounds. The data of Li\textsuperscript{7}RuO\textsubscript{6} are reproduced from ref. [7]. The data of NiGa\textsubscript{2}S\textsubscript{4} are estimated from Fig. 4(b) using the experimental \( T_{1} \) values in ref. [13]. The data of KCrO\textsubscript{2} are reproduced from ref. [19]. \( J_{\Theta} \) of LiCrO\textsubscript{2} is from refs. [1, 4].

|           | \( 4\pi\rho_{s} \) (K) | \( J_{s} \) (K) | \( J_{\Theta} \) (K) |
|-----------|------------------------|-----------------|-----------------|
| Li\textsuperscript{7}RuO\textsubscript{6} | 40                     | 2.1             | 9.7             |
| NiGa\textsubscript{2}S\textsubscript{4} | 68                     | 9.5             | 20              |
| KCrO\textsubscript{2}       | 130                    | 9.3             | 29              |
| LiCrO\textsubscript{2}       | —                      | —               | 80              |

Figure 4(a) shows semi-logarithmic plot of \( 1/ T_{1} T^{3} \) against inverse temperature \( 100/ T \) for LiCrO\textsubscript{2}. The dash curve is \( 1/ T_{1} = 1/ T_{1\infty} \). The solid curve is a best fit result of \( 1/ T_{1} \propto (T/ T_{N} - 1)^{-w} \) near \( T_{N} \). No trace of two dimensional renormalized classical regime is found.

For comparison, Fig. 4(b) shows semi-logarithmic plots of \( 1/ T_{1} T^{3} \) against inverse temperature \( 10/ T \) for Li\textsuperscript{7}RuO\textsubscript{6} [7] and NiGa\textsubscript{2}S\textsubscript{4} [13]. The solid lines are the best fit results of \( 1/ T_{1} T^{3} \propto \exp(4\pi\rho_{s}/ T) \), which is characteristic of the two dimensional renormalized classical behavior of the triangular lattice spin systems.

Since the solid lines in Fig. 4(b) well fit the experimental \( 1/ T_{1} \) at low temperatures, the spin-spin correlations of Li\textsuperscript{7}RuO\textsubscript{6} [7] and NiGa\textsubscript{2}S\textsubscript{4} [13] are in the two dimensional renormalized classical regimes. However, the exchange coupling constants \( J_{s} \)’s estimated from eqs. (2) and (3) are smaller than the exchange constants \( J_{\Theta} \)’s estimated from the Curie-Weiss susceptibility fit at higher temperatures [20]. The estimated parameters of \( 4\pi\rho_{s}, J_{s} \) and \( J_{\Theta} \) are listed in Table 1. One may find \( J_{s} \sim J_{\Theta}/5 \) for Li\textsuperscript{7}RuO\textsubscript{6}, \( J_{s} \sim J_{\Theta}/2 \) for NiGa\textsubscript{2}S\textsubscript{4}, and \( J_{s} \sim J_{\Theta}/3 \) for KCrO\textsubscript{2}. Since no frustration effects are taken into consideration in eq. (3), the reason of \( J_{s} < J_{\Theta} \) can be traced back to the spin frustration effects on a spin-spin correlation function at a low frequency. Actually, the reduction of the spin stiffness constant \( \rho_{s} \) due to the spin frustration (\( Z_{2} \) vortices) is seen in the numerical studies of Heisenberg frustrated spin systems [21].

5. Conclusions

We have made a detailed experimental study of the \( ^{7}\text{Li} \) NMR FID signal in the paramagnetic state of the triangular lattice antiferromagnet LiCrO\textsubscript{2}. The critical behavior of the \( ^{7}\text{Li} \) nuclear spin-lattice relaxation rate \( 1/ T_{1} \) of the FID signal near \( T_{N} \) is found to be well described by a power law. The critical exponent takes \( w = 0.45 \). The narrow critical region and no trace of two dimensional renormalized classical regime are found. The three dimensional exchange interaction may play a central role in the critical behavior of LiCrO\textsubscript{2}.

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