μ⁺SR study on triangular antiferromagnet LiCrO₂

Y Ikedo¹, J Sugiyama², K Mukai², M Månsson³, T Goko⁴, D Andreica⁵ and A Amato⁶

¹ Muon Science Laboratory, KEK, Ibaraki, Japan
² Toyota Central R&D Laboratories Inc., Aichi, Japan
³ LNS, ETH Zurich and Paul Scherrer Institut, Villigen PSI, Switzerland
⁴ TRIUMF, Vancouver, Canada
⁵ Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania
⁶ Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, Villigen PSI, Switzerland

E-mail: e0589@mosk.tytlabs.co.jp

Abstract. In order to elucidate the magnetic nature of the lithium chromium dioxide LiCrO₂, in which the Cr³⁺ ions form a two-dimensional triangular lattice in the CrO₂ plane, we have performed a positive muon-spin rotation and relaxation (μ⁺SR) experiment using a powder sample at the temperatures below 155 K. Weak-transverse-field measurements indicated the existence of a bulk antiferromagnetic (AF) transition at \(T_N=61.2\) K. The ZF-μ⁺SR measurements indicated that LiCrO₂ is a pure paramagnet for \(T<5\) K, since its internal magnetic field (\(H_{int}\)) can be explained by solely nuclear magnetic moments. This means that, contrary to previous suggestions by susceptibility and heat capacity measurements, no short-range order exists for \(T<62\) K. However, ZF-μ⁺SR detected the change in \(H_{int}\) from a low-T static state to a high-T dynamic state at 115 K, most likely connected to a change in the position/motion of the Li ions.

1. Introduction

Historically the two-dimensional triangular lattice (2DTL) system has served as a playground for novel ideas about unconventional phases of frustrated anti-ferromagnets. The layered cobalt/nickel oxides has been heavily investigated e.g. LiCoO₂ (electrode in Li-ion batteries) and NaₓCoO₂ (thermoelectric properties and superconductor) [1, 2, 3]. However, experimental studies on the chromium dioxides have been very limited. Recently a newfound interest has started as shown by both experimental [4] and theoretical work [5].

For LiNiO₂ [2] and Na₀.75CoO₂ [6], an A-type antiferromagnetic (AF) order is present at low temperature, with ferromagnetic (FM) order within the NiO₂ planes and AF order between the planes. However, for LiCrO₂, experimental work [7], as well as theoretical studies [5], show that the intraplane magnetic interaction is strongly AF, while the interplane is very weak and also AF. Susceptibility (\(\chi\)) data [7] show clear AF order below \(T_N=62\) K. Further, \(\chi(T)\) curve does not follow Curie-Weiss law below 300 K [8]. This Indicates that a possible short-range order sets in well above \(T_N\). However, no experimental study is to be found in the published literature.

As we reported in previous paper [10], wTF measurements indicated the existence of a bulk AF transition at \(T_N=61.2\) K (see Fig 2). Below \(T_N\), ZF-μ⁺SR spectra showed a clear spontaneous oscillation, indicating the formation of static long-range order. The observed ZF-spectrum was well reproduced by the AF spin structure proposed by neutron measurements [11]. In this
Figure 1. Crystal structure of LiCrO$_2$ showing (a) alternating stacks of Li and CrO$_2$ layers along the $c$-axis and (b) top-view along the $c$-axis demonstrating the triangular configuration of the Cr-ions.

Figure 2. Temperature dependence of the wTF (= 30 Oe) $\mu^+\text{SR}$ time spectra. $A_0$ is the initial ($t=0$) asymmetry and $P_{TF}(t)$ is the muon spin polarization function. These spectra show a clear decrease of the $A_0$ between 61 K and 62.5 K, indicating the existence of AF transition.

In this paper, we mainly report the $\mu^+\text{SR}$ experiment on LiCrO$_2$ above $T_N$, in order to clarify the non Curie-Weiss behavior in $\chi(T)$ curve for LiCrO$_2$.

2. Experimental Details
A powder sample of LiCrO$_2$ was prepared at Osaka City University by a solid-state reaction technique using reagent grade LiOH-H$_2$O and Cr$_2$O$_3$ powders as starting materials. Powder x-ray diffraction (XRD) analysis showed that the sample was single phase with a rhombohedral system of space group $R\overline{3}m$; the $a_{\text{H}}$-axis length was 2.899 Å and the $c_{\text{H}}$-axis length was 14.418 Å. An inductively coupled plasma (ICP) analysis indicated that the Li/Cr ratio was 1.03.

$\mu^+\text{SR}$ spectra were measured at the Swiss Muon Source ($\text{S}\mu\text{S}$), Paul Scherrer Institut, Villigen, Switzerland. By using the surface muon beamline $\mu$E1 and the Dolly spectrometer, zero-field (ZF), weak transverse-field (wTF), and weak longitudinal-field (LF) spectra were collected for 1.7 K $\leq T \leq$ 155 K. The experimental setup and techniques were described in detail elsewhere [9].
3. Experimental Results

The ZF-spectrum exhibits a Kubo-Toyabe behavior just above \( T_N \) [see Fig. 3(a)]. This means that the implanted muons see the internal magnetic field (\( H_{\text{int}} \)) due to nuclear magnetic moments of \( ^{7}\text{Li} \) and \( ^{6}\text{Li} \), together with a minor contribution from \( ^{53}\text{Cr} \). Contrary to previous suggestions [8], this also excludes the possibility of the formation of any short-range order above \( T_N \). However, as \( T \) increases from 80 K, the minimum in the ZF spectrum (\( \sim 6 \) \( \mu \)s at 80 K) shifts towards a later time domain and the relaxation rate decreases with \( T \). This implies that \( H_{\text{int}} \) starts to fluctuate above 80 K. Indeed, the ZF-spectrum are well fitted by a dynamic Gaussian Kubo-Toyabe function \( G^{\text{DGKT}}(\Delta, \nu, t) \) for \( H_{\text{int}} \) due to the fluctuating nuclear magnetic moments;

\[
A_0 P_{ZF,LF}(t) = A_{KT} G^{\text{DGKT}}(\Delta, \nu, t),
\]

where \( \Delta \) is the static width of the local frequency at the disordered sites, and \( \nu \) is the field fluctuation rate. A preliminary fit using Eq. (1) for the ZF-spectrum at each \( T \) between 62.5 and 155 K indicated that the two parameters, \( A_{KT} \) and \( \Delta \), are approximately independent of \( T \). All of the ZF-spectra were, therefore, fitted by Eq. (1) using common \( A_{KT} \) and \( \Delta \). The global fit provides that \( A_{KT} = 0.2309 \pm 0.0002 \) and \( \Delta = (0.3124 \pm 0.0001) \times 10^6 \text{ s}^{-1} \).

Figure 3(b) shows the \( T \) dependence of \( \nu \) for LiCrO\(_2\) together with the \( T \)-independent \( \Delta_{\text{PM, measure}} \). The \( \nu(T) \) curve shows a dull but step-like change from almost 0 to \( \sim 0.96 \times 10^6 \text{ s}^{-1} \) in the \( T \) range between 80 and 140 K. This demonstrates the appearance of dynamical fluctuation of \( H_{\text{int}} \) above \( \sim 80 \) K. In addition, weak longitudinal field (\( LF = 20 \text{ Oe} \)) measurements at 65 K and 140 K supports the \( \nu(T) \) and \( \Delta(T) \) curve obtained by the global fit for the ZF-spectra. Moreover, the \( \chi_{\text{ZFC}}(T) \) curve starts to deviate from the \( \chi_{\text{ZFC}}(T) \) curve below approximately 130 K [10]. This evidences the intrinsic change in a magnetic environment of LiCrO\(_2\) around 130 K. Therefore, it is very reasonable to consider the change in Li motion/position as an origin of the increase in \( \nu \) above 80 K.

4. Discussion

According to electrostatic potential calculations, positive muons are most likely to locate in the vicinity of the \( \text{O}^{2-} \) ions; that is, \( \sim 1 \) Å away from the \( \text{O}^{2-} \) ions along the \( c \)-axis. Taking into account the nuclear magnetic moments of \( ^{7}\text{Li} \), \( ^{6}\text{Li} \), and \( ^{53}\text{Cr} \), the dipole field calculations at muon site in the paramagnetic state provided that \( \Delta_{\text{PM,calc}}^{\text{PM}} = (0.485 \pm 0.002) \times 10^6 \text{ s}^{-1} \). This is roughly in agreement with the experimental result, although the calculated \( \Delta_{\text{PM,calc}}^{\text{PM}} \) is 55% larger [see Fig. 3(b)] than the measured \( \Delta_{\text{PM,measure}}^{\text{PM}} \)\( \approx (0.3124 \pm 0.0001) \times 10^6 \text{ s}^{-1} \). Consequently, the \( \Delta \), which are predicted by the electrostatic potential calculations, are found to give reasonable \( H_{\text{int}} \) both for the AF ordered state and the paramagnetic state.

The \( \nu(T) \) curve demonstrates a clear change of \( H_{\text{int}} \) from a low-\( T \) static state to a high-\( T \) dynamic state at \( T_c \sim 115 \) K, at which \( \nu = \frac{1}{2}[\nu(65 \text{ K}) + \nu(155 \text{ K})] \). Since \( \nu \) appears to level off to a constant value above 140 K [see dotted curve in Fig. 3(b)], the change at \( T_c \) is most unlikely due to a diffusive motion of the Li\(^{+} \) ions. This is because the relationship between \( \nu \) and \( T \) is expected to be given by \( \nu \propto \exp(-1/T) \) for Li diffusion [12]. Therefore, \( T_c \) is more likely to be associated with a structural transition caused by the change in the position of Li\(^{+} \) ions. In other words, \( T_c \) could be explained by an order-disorder transition of the Li\(^{+} \) ions; i.e., the Li ions could slightly shift their position from the regular site at low \( T \). Moreover, \( \Delta \) is expected to be insensitive to such small displacement of the Li\(^{+} \) ions, when the Li\(^{+} \) ions locate in the vicinity of the regular Li site.

Such transition would induce a charge disproportionation of the Cr ions; i.e., \( \text{Cr}^{3+} \rightarrow \text{Cr}^{3+/6+} + \text{Cr}^{3-} \), as in the case for Na\(_{0.5}\)CoO\(_2\) [13, 14]. However, even for the mixed valence state of the Co ions in Na\(_{0.5}\)CoO\(_2\), \( \delta \) was reported below 0.2 [13, 14]. Hence, it would be very difficult to detect \( \delta \) for LiCrO\(_2\), even if such charge disproportionation occurs.
Figure 3. Temperature dependences of (a) ZF-μSR spectrum above $T_N$ and (b) the field distribution width ($\Delta$) shown as triangles and field fluctuation rate ($\nu$) as circles. The data in (b) were obtained by fitting the $\mu^+$SR time spectra to Eq. (1). Closed symbols are obtained from a global fit to ZF-spectra only, while open symbols are obtained from a global fit to both ZF and longitudinal field (LF = 20 Oe) spectra at 65 and 140 K. The solid horizontal line in (b) represents a common $\Delta_{\text{PM}}$ measure ($= 0.3124 \times 10^6$ s$^{-1}$) for a global fit, while the dashed horizontal line shows a prediction from dipole field calculations $\Delta_{\text{calc}}$. Dotted curve serves as a guide to the eye.

Actually, although we attempted to fit the ZF-spectrum by $G^{DGKT}(\Delta, \nu, t) \exp(-\lambda_{C^t}t)$, where the exponential relaxation should correspond to the fluctuation of the Cr spins, the $\lambda_{C^t}(T)$ curve exhibits no crucial anomaly around $T_c$. It should also be noted that a Kubo-Toyabe function is only an approximation of the nuclear dipole contribution to the ZF-μSR spectrum. Hence, although the spectrum is well fitted by a Kubo-Toyabe function, there is still a possibility that the dynamics observed above $T_N$ originate from electronic moments. In order to further investigate the details of this transition, we need to measure the ZF- and LF-spectra at high $T$ using a pulse-muon facility, such as, ISIS in the UK or J-PARC in Japan. Furthermore, it is more preferable to perform a precise structural analysis of LiCrO$_2$ as a function of $T$ by both neutron and x-ray (from a synchrotron radiation source) diffraction.

Finally, we wish to address the possible role of the order-disorder transition of the Li ions for the magnetic nature of LiCrO$_2$. In contrast to NaCrO$_2$, for which no long-range AF order is observed by neutron measurements down to the lowest $T$ measured [15, 16], a long-range AF order is clearly detected in LiCrO$_2$ by neutron measurements [11], for reasons currently...
unknown. As in the case for Na$_{0.5}$CoO$_2$ [17, 18] and K$_{0.5}$CoO$_2$ [19, 20], the Li ordering in LiCrO$_2$ below 115 K is expected to alter the charge distribution within the CrO$_2$ planes, and could hereby stabilize the long-range order below $T_N$. Also, since the Kubo-Toyabe behavior is observed for $T \geq 62.5$ K, it is most unlikely that (previously suggested) short-range order is present above $T_N$ in LiCrO$_2$. In order to explain non Curie-Weiss behavior of the $\chi(T)$ curve at high $T$, we thus need another mechanisms; such as, a Li disordering above 115 K inducing slight delocalization of the charge/spin state of the Cr ions, resulting in the difference between the $\chi_{ZFC}(T)$ and $\chi_{ZFC}(T)$ curve below 130 K. Also, such Li disordering would provide an additional contribution to $C_p$, which is probably difficult to distinguish from a magnetic contribution by only subtracting $C_p$ for LiCoO$_2$ from $C_p$ for LiCrO$_2$ [8], as in the case for Na$_{0.62}$CoO$_2$ [21].

5. Conclusions
By means of a positive muon-spin rotation and relaxation ($\mu^+SR$) technique, we have clarified the magnetic nature of LiCrO$_2$, in which the Cr$^{3+}$ ions form a two-dimensional triangular lattice in the CrO$_2$ plane. Below $T_N = 61.2$ K, zero-field (ZF-) $\mu^+SR$ measurements demonstrate the formation of static AF order. The observed ZF-spectrum was well explained by the AF spin structure proposed by neutron measurements. Furthermore, the ZF-$\mu^+SR$ measurements clearly indicated the absence of magnetic-order for $T \geq 62.5$ K, whether it is long-ranged or short-ranged. Instead, a dynamic change in the Li motion was detected at approximately $T = 115$ K, probably due to an order-disorder transition within the Li planes.

Acknowledgments
This work was performed at the Swiss Muon Source, Paul Scherrer Institut, Villigen, Switzerland and we are thankful to Robert Scheuermann for assistance with the SR experiments. YI and JS are partially supported by the KEK-MSL Inter-University Program for Overseas Muon Facilities. This work is also supported by Grant-in-Aid for Scientific Research (B), 19340107, MEXT, Japan. All images involving crystal structure were made with VESTA.

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