\( \mu^+ \text{SR} \) investigation of local magnetic order in LiCrO\(_2\)

Jun Sugiyama,1,⋆ Martin Månsson,2 Yutaka Ikedo,1,† Tatsuo Goko,3 Kazuhiko Mukai,1 Daniel Andreica,4 Alex Amato,5 Kingo Ariyoshi,6 and Tsutomu Ohzuki6

1Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan
2Laboratory for Neutron Scattering, ETH Zürich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
3TRIUMF, 4004 Wesbrook Mall, Vancouver, British Columbia, Canada V6T 2A3
4Faculty of Physics, Babes-Bolyai University, 3400 Cluj-Napoca, Romania
5Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
6Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Osaka 558-8585, Japan

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In order to elucidate the magnetic nature of the lithium chromium dioxide LiCrO\(_2\), in which the Cr\(^{3+}\) ions form a two-dimensional triangular lattice in the CrO\(_2\) plane, we have performed a positive muon-spin rotation and relaxation (\( \mu^+ \text{SR} \)) experiment using a powder sample in the temperature range 1.7–155 K. Weak-transverse-field measurements indicated the existence of a bulk antiferromagnetic (AF) transition at \( T_N = 61.2 \) K. Below \( T_N \), zero-field (ZF) \( \mu^+ \text{SR} \) measurements demonstrated the formation of static long-range order; the observed ZF spectrum was well reproduced by the AF spin structure proposed by neutron measurements. The ZF-\( \mu^+ \text{SR} \) measurements also indicated that LiCrO\(_2\) is a pure paramagnet for \( T \approx 62.5 \) K, since its internal magnetic field (\( H_{\text{int}} \)) 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 \( T \geq 62.5 \) K. However, ZF-\( \mu^+ \text{SR} \) detected the change in \( H_{\text{int}} \) 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.

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I. INTRODUCTION

In nonbipartite lattices such as the triangular one, in the case of half-filling the Hubbard model has an extraordinarily rich ground-state structure including a paramagnetic phase, different long-range orders, and also metal-insulator transitions. Historically the triangular lattice system has served as a playground for new ideas about various unconventional phases of frustrated antiferromagnets.1

In this context, the layered cobalt dioxides have been the center of attention for many years.2,3 The two main driving forces have been the electrochemical importance of the LiCoO\(_2\) compound as an electrode in Li-ion batteries,4 and by the unconventional superconductivity discovered in the Na\(_0.35\)CoO\(_2\) · 1.3H\(_2\)O compound.5 Further, the layered nickel dioxides, e.g., LiNiO\(_2\),6 NaNiO\(_2\),20,21 and Na\(_{0.75}\)CoO\(_2\),22,23 an A-type antiferromagnetic (AF) order is present at low \( T \), with ferromagnetic (FM) order within the Ni/Co planes and AF order between the planes. The intraplane FM order naturally comes from superexchange along the 90° O-Ni/Co-O bond angle. The O-Cr-O bond angle is also close to 90°, hence the same intraplane FM order could be expected. However, experimental work regarding NaCrO\(_2\) (Ref. 16) and LiCrO\(_2\) (Ref. 9), as well as theoretical studies of LiCrO\(_2\) (Ref. 17) show, in agreement, that the intraplane magnetic interaction is strongly AF, while the interplane is very weak and also AF.

The crystal structure of LiCrO\(_2\) was reported to be an \( \alpha\)-NaFeO\(_2\)-type rhombohedral system of space group \( R3m \) (\( a_0 = 2.9010 \) Å, \( c_0 = 14.4311 \) Å).19 Here, \( a_0 \) denotes the \( a \)-axis length of the CrO\(_2\) plane in hexagonal setting. In this structure, single CrO\(_2\) sheets and single disordered Li planes form alternating stacks along the hexagonal \( c \) axis (see Fig. 1). Its magnetic structure is close to the ideal 120° structure characteristic of the nearest-neighbor Heisenberg model on a two-dimensional triangular lattice (2DTL). The Cr ions are expected to have a valence +3 and to be in a \( S = \frac{3}{2} \) spin state, although the valence state of the Cr ions would be affected by structural distortion of the LiCrO\(_2\) lattice. For LiNiO\(_2\),6 NaNiO\(_2\),20,21 and Na\(_{0.35}\)CoO\(_2\),22,23 an A-type antiferromagnetic (AF) order is present at low \( T \), with ferromagnetic (FM) order within the Ni/Co planes and AF order between the planes. The intraplane FM order naturally comes from superexchange along the 90° O-Ni/Co-O bond angle. The O-Cr-O bond angle is also close to 90°, hence the same intraplane FM order could be expected. However, experimental work regarding NaCrO\(_2\) (Ref. 16) and LiCrO\(_2\) (Ref. 9), as well as theoretical studies of LiCrO\(_2\) (Ref. 17) show, in agreement, that the intraplane magnetic interaction is strongly AF, while the interplane is very weak and also AF.

FIG. 1. (Color online) 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.
The explanation to this difference is to be found in the enhanced direct overlap between the metal $d$ orbitals in layered chromium dioxides. Indeed there exists a driving force toward FM intraplane order through superexchange via the $\sim 94^\circ$ O-Cr-O bond. However, the large direct $p-d$ overlap of Cr surpasses the superexchange and instead drives the intraplane order to be AF. This has been shown to be true by experimental\textsuperscript{9} as well as theoretical\textsuperscript{17} work. In addition, it has also been shown that the increased charge-transfer $p-d$ gap reduces the ferromagnetic superexchange in layered chromium dioxides, further strengthening the AF order within the Cr planes.

From susceptibility measurements, electronic paramagnetic resonance, and Mössbauer spectroscopy\textsuperscript{9,24,25} it has been shown that a clear long-range AF order sets in below $T_N=62$ K. Further, the same bulk susceptibility data show that this compound does not follow Curie-Weiss law below approximately 300 K.\textsuperscript{25} This could indicate that a possible short-range order sets in well above $T_N$ and long-range order is finally achieved for $T\leq T_N$. Some support for this statement could be found in heat capacity ($C_p$) measurements\textsuperscript{25} that shows a contribution to magnetic entropy all the way up to $T=4T_N$. However, to the author’s knowledge, there has been no direct experimental evidence of short-range order and in fact no experimental study is to be found in the published literature regarding the microscopic magnetic nature of LiCrO$_2$.

The positive muon-spin rotation and relaxation ($\mu^+\text{SR}$) technique has during the last 30 years been established as a powerful method to study local magnetic fields and spin order in a wide range of materials.\textsuperscript{26–28} By implanting highly spin polarized muons ($S=\frac{1}{2}$) into a material and monitoring the angular and temporal decay into positrons, the muon acts as a unique and highly localized magnetic probe. Contrary to other magnetic resonance techniques (e.g., NMR), $\mu^+\text{SR}$ is the only technique that can directly probe an internal magnetic field caused by magnetic order/moments without any externally applied field. In this paper, we present a first principal study of microscopic magnetic order and transitions in this 2DTL material using zero-field (ZF) as well as weak transverse-field (wTF) $\mu^+\text{SR}$.

II. 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. A mixture of the two powders was heated at 1000 °C for 12 h in an air flow. Powder x-ray diffraction analysis showed that the sample was single phase with a rhombohedral system of space group $R\bar{3}m$; the $a_H$-axis length was 2.899 Å and the $c_H$-axis length was 14.418 Å. An inductively coupled plasma analysis indicated that the Li/Cr ratio was 1.03.

The pressed powder was placed in a small envelope made of very thin Al-coated Mylar tape and then attached to a low-background fork-type sample holder. In order to stop the muons primarily inside the sample, we made sure that the side facing the muon beamline was only covered by a single layer of Mylar tape. Subsequently, $\mu^+\text{SR}$ spectra were measured at the Swiss Muon Source ($S\mu S$), Paul Scherrer Institut, Villigen, Switzerland. By using the surface muon beamline $\mu$E1 and the Dolly spectrometer, ZF, 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.\textsuperscript{29}

The magnetic susceptibility ($\chi$) of the sample was measured using a superconducting quantum interference device magnetometer (MPMS, Quantum Design) in the $T$ range between 400 and 5 K under magnetic field $H=\leq 10$ kOe. As seen in Fig. 2, $\chi(T)$ data from the present sample reproduce the prior measurements reported in Refs. 9, 12, and 25.

III. EXPERIMENTAL RESULTS

A. Overall feature by wTF-$\mu^+\text{SR}$

Figure 3 shows the variation in the wTF time spectra acquired at different temperatures. When $T$ decreases below

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2}
\caption{Temperature dependence of (a) magnetic susceptibility ($\chi$) and (b) inverse $\chi$ for the powder sample of LiCrO$_2$. $\chi$ was measured in field-cooling (FC) mode with magnetic field $H=10$ kOe.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3}
\caption{(Color online) Temperature dependence of the wTF($=30$ Oe) $\mu^+\text{SR}$ time spectra. Solid lines represent the fitting result using Eq. (1).}
\end{figure}
In order to demonstrate the formation of static magnetic order below $T_N$, Fig. 5 shows the $T$ dependence of ZF-$\mu^*$SR

\begin{align}
A_0 P_{TF}(t) &= A_{TF} \cos(\omega_{TF} t + \phi_{TF}) \exp(-\lambda_{TF} t) \\
&+ A_{fast} \exp(-\lambda_{fast}),
\end{align}

where $A_0$ is the initial ($t=0$) asymmetry, $P_{TF}(t)$ is the muon spin polarization function, $\omega_{TF}$ is the muon Larmor frequency corresponding to the applied $wTF$, $\phi_{TF}$ is the initial phase of the precessing signal, $\lambda_{TF}$ and $\lambda_{fast}$ are the exponential relaxation rates, and $A_{TF}$ and $A_{fast}$ are the asymmetries of the two components of the $\mu^*$SR spectrum. This form was chosen because the externally applied magnetic field is much weaker than the local (internal) magnetic fields in the ordered phase. By plotting $A_{TF}$ versus $T$ [see Fig. 4(a)], we can clearly see that the sample has a bulk magnetic transition at $T_N=61.2$ K, where the normalized $A_{TF}/A_0 = N_{A_{TF}}$ has a nonzero value below $T_N$ and increases with decreasing $T$, and finally levels off to $\sim 0.2$ below 50 K. The fact that $N_{A_{fast}}$ never reaches the full asymmetry ($\approx 1$) suggests the presence of a fast relaxing/precessing signal in the wTF spectrum. However, in order to distinguish such a signal, the ZF-$\mu^*$SR technique with high statistics is more suitable.

B. ZF-$\mu^*$SR below $T_N$

In order to demonstrate the formation of static magnetic order below $T_N$, Fig. 5 shows the $T$ dependence of ZF-$\mu^*$SR

FIG. 5. (Color online) Temperature-dependent ZF-$\mu^*$SR spectra for LiCrO$_2$. Solid lines represent the fitting result using Eq. (2). Each spectrum is offset by 0.1 for clarity of display.

FIG. 4. Temperature dependences of (a) normalized asymmetries ($A_{TF}$ and $A_{fast}$), (b) exponential relaxation rates ($\lambda_{TF}$ and $\lambda_{fast}$), and (c) magnetic susceptibility ($\chi$). The data in (a) and (b) were obtained by fitting the wTF spectra using Eq. (1). $\chi$ was measured both in FC and zero-field-cooling (ZFC) mode with magnetic field $H=100$ Oe.

62.5 K, the oscillation amplitude due to wTF rapidly decreases, indicating the appearance of additional strong internal magnetic field(s) ($H_{int}$). The wTF-$\mu^*$SR spectrum was consequently fitted using a combination of a slowly relaxing precessing signal and a fast relaxing nonoscillatory signal. The first component is due to the externally applied magnetic field (wTF=30 Oe) and the second due to $H_{int}$.

$A_0 P_{TF}(t) = A_{TF} \cos(\omega_{TF} t + \phi_{TF}) \exp(-\lambda_{TF} t) + A_{fast} \exp(-\lambda_{fast}).$
time spectrum in the $T$ range between 1.7 and 62.5 K. Below $T_N$, muon spins are clearly precessing due to the appearance of a spontaneous $H_{\text{int}}$, resulting in a clear oscillation in the ZF-$\mu^S$SR spectrum. The ZF spectrum was well fitted by the combination of two damped cosine oscillations, which are originating from the static ordered $H_{\text{int}}$, and a slowly relaxing nonoscillatory signal due to the “1/3 tail” caused by the field components parallel to the initial muon-spin polarization:

$$A_0 P_{ZF}(t) = A_{AF1} \exp(-\lambda_{AF1} t)\cos(\omega_{AF1}^\mu t + \phi_1) + A_{AF2} \times \exp(-\lambda_{AF2} t)\cos(\omega_{AF2}^\mu t + \phi_2) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t).$$

(2)

Here, $A_0$ is the initial ($t=0$) asymmetry, $P_{ZF}(t)$ is the muon-spin polarization function in ZF, $\omega_{AF1}^\mu$ and $\omega_{AF2}^\mu$ are the two muon Larmor frequencies corresponding to the ordered $H_{\text{int}}$, $\phi_1$ and $\phi_2$ are the initial phases of the precessing signals, $\lambda_{AF1}$ and $\lambda_{AF2}$ are the exponential relaxation rates of the precessing signals, $\lambda_{\text{tail}}$ is the exponential relaxation rate of the tail signal, and $A_{AF1}$, $A_{AF2}$, and $A_{\text{tail}}$ are the asymmetries of the three signals.

The fit for the ZF spectrum at the lowest $T$ measured (1.7 K) yields $\phi_1 = 48 \pm 6^\circ$ and $\phi_2 = 52 \pm 7^\circ$. This indicates that, although Eq. (2) well reproduces the obtained ZF spectrum as seen in Fig. 5, it is too simple for describing $H_{\text{int}}$ in the AF ordered state. In other words, this implies the formation of a complex AF structure, as in the case for NaV$_2$O$_4$ (Ref. 30), because $\phi_1$ should be zero for a simple commensurate AF order. Indeed, neutron measurements proposed a double-$Q$ 120° structure with two different wave numbers $q = (\frac{1}{3}, \frac{1}{3}, 0)$ and $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$. This means the presence of a wide distribution of $H_{\text{int}}$ at the muon sites (see Sec. IV A). However, since the determined AF spin structure is commensurate to the lattice, it is reasonable to fix $\phi_1 = \phi_2 = 0$. Actually, when we use a common $\phi = (\phi_1 = \phi_2)$ in Eq. (2), we obtain $\phi = -8 \pm 3^\circ$ (eventually 0), as expected. The other $\mu^S$SR parameters at 1.7 K, when we fix $\phi = 0$, are obtained as $A_{AF1} = 0.108 \pm 0.002$, $A_{AF2} = 0.073 \pm 0.002$, $A_{\text{tail}} = 0.059$, $f_{AF1} = \omega_{AF1}^\mu / 2\pi = 24.3 \pm 0.6$ MHz, $f_{AF2} = \omega_{AF2}^\mu / 2\pi = 41.9 \pm 0.3$ MHz, $\lambda_{AF1} = (52 \pm 3) \times 10^6$ s$^{-1}$, $\lambda_{AF2} = (30 \pm 2) \times 10^6$ s$^{-1}$, and $\lambda_{\text{tail}} = (0.037 \pm 0.002) \times 10^6$ s$^{-1}$. Note that we fixed the total asymmetry as 0.24, i.e., $A_{AF1} + A_{AF2} + A_{\text{tail}} = 0.24$. Since the preliminary fit at each $T$ indicated that $A_{AF1}$, $A_{AF2}$, $A_{\text{tail}}$, and $\phi$ was almost $T$ independent except below the vicinity of $T_N$, we attempted to fit all the ZF spectra below $T_N$ using common $A_{AF1}$, $A_{AF2}$, $A_{\text{tail}}$, and $\phi = 0$, i.e., a global fit technique.

Figure 6 shows the $T$ dependences of the $\mu^S$SR parameters obtained by a global fit with common $A_{AF1} = 0.10678 \pm 0.00013$, $A_{AF2} = 0.07424 \pm 0.00013$, and $A_{\text{tail}} = 0.05898$. Here $A_{\text{tail}}$ is approximately only 3/4 of the expected value for the tail (0.24/3), most probably due to preferred orientation caused by pressing of the LiCrO$_2$ powder. Making comparison with the result of the xTF measurements, $A_{AF1}$ is almost equivalent to $A_{\text{tail}}$, which should correspond to the 1/3 tail signal. This clearly supports the above assignment for the $A_{\text{tail}}$ signal.

The two $f_{AF}(T)$ curves exhibit an order-parameter-like $T$ dependence, although it is difficult to evaluate a critical exponent $[\beta$ for $f/f_{T=0} = (1 - T_N/T)^\beta]$ due to a lack of data points just below $T_N$. As $T$ increases from 1.7 K, the two $f_{AF}$’s seem to disappear simultaneously at $T_N$. This clearly suggests that the two $f_{AF}$’s are not caused by the coexistence of two different phases in the sample but rather by two magnetically inequivalent muon sites in the lattice (see Sec. IV A).

The $\lambda_{AF1}$ decreases slowly with increasing $T$, but increases again below the vicinity of $T_N$, indicating an increase toward a wider field distribution near $T_N$. As a result, it is difficult to obtain accurate $f_{AF1}$ in the $T$ range between 60 and $T_N$. In contrast, the $\lambda_{AF2}(T)$ curve is almost $T$ independent up to $T_N$. Finally, the magnitude of $\lambda_{\text{tail}}$ remains below $1.4 \times 10^6$ s$^{-1}$ in the whole $T$ range measured. Although $\lambda_{\text{tail}}$ increases with $T$, its value is 2 orders of magnitude smaller than $\lambda_{AF1}$ and $\lambda_{AF2}$. Furthermore, $\lambda_{\text{tail}}$ approaches 0, when $T \rightarrow 0$. Therefore, it is very reasonable to assign this signal as a 1/3 tail signal.

C. ZF-$\mu^S$SR above $T_N$

The ZF spectrum exhibits a Kubo-Toyabe behavior just above $T_N$ [see Fig. 7(a)]. This means that the implanted muons see the internal magnetic field ($H_{\text{int}}$) only due to the nuclear magnetic moments of $^7$Li and $^6$Li, together with a minor contribution from $^{53}$Cr. Contrary to previous
where \( s \) spectrum

However, as 

\( A_0 \) is well fitted by a dynamic Gaussian Kubo-Toyabe function 

suggestions,\(^{25}\) this finding excludes the possibility of the formation of any short-range order above \( T_N \). In other words, the AF transition is very sharp and continuous, as expected. However, as \( T \) increases from 80 K, the minimum in the ZF spectrum (\( \sim 6 \) \( \mu \)s at 80 K) shifts toward 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 is well fitted by a dynamic Gaussian Kubo-Toyabe function 

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

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. (3) for the ZF spectrum at each \( T \) between 62.5 and 155 K indicated that the two parameters, \( A_{\text{KT}} \) and \( \Delta \), are approximately independent of \( T \). All of the ZF spectra were, therefore, fitted by Eq. (3) using common \( A_{\text{KT}} \) and \( \Delta \). The global fit provides that \( A_{\text{KT}} = 0.2309 \pm 0.0002 \) and \( \Delta = 0.3124 \pm 0.0001 \) \( \times 10^6 \) s\(^{-1}\).

Figure 7(b) shows the \( T \) dependence of \( \nu \) for LiCrO\(_2\) together with the \( T \)-independent \( \Delta_{\text{measure}} \). The \( \nu(T) \) curve shows a dull but steplike change from almost 0 to \( \sim 0.96 \times 10^6 \) 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 \( \approx 20 \) Oe) measurements at 65 and 140 K supports the \( \nu(T) \) and \( \Delta(T) \) curve obtained by the global fit for the ZF spectra. Moreover, the \( \chi_{\text{FC}}(T) \) curve starts to deviate from the \( \chi_{\text{ZF}}(T) \) curve below approximately 130 K [see Fig. 4(c)]. 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. The detail of the \( T \) dependence of \( \nu \) will be discussed in Sec. IV B.

**IV. DISCUSSION**

**A. Muon sites and \( H_{\text{int}} \)**

According to electrostatic potential calculations, positive muons are most likely to locate in the vicinity of the \( O^2^- \) ions; that is, \( \sim 1 \) Å away from the \( O^2^- \) ions along the \( c \) axis. Further, assuming the AF spin structure, i.e., the double-\( Q \) 120° structure, proposed by neutron measurements,\(^{12}\) there exist 36 magnetically different muon sites, although there is crystallographically only one muon site in the LiCrO\(_2\) lattice. This is because the magnetic unit cell is reported to be three times larger than the crystallographic unit cell. Also, due to the helical spin structure along the \( c \) axis, the muon site above a certain \( O^2^- \) ion is magnetically different from that below the \( O^2^- \) ion. Since there are 6 oxygen in the crystallographic unit cell for \( Z=3 \), the total number of the muon sites is provided by \( 6 \times 2 \times 3 = 36 \).

Dipole field calculations for the 36 muon sites yielded a field distribution shown in Fig. 8(a) at the muon sites for the AF ordered state. The ZF-\( \mu \)SR time spectrum is thus given by

\[ P_{\text{ZF}}(t) = \frac{2}{3} \sum_{i=1}^{36} \cos(2\pi f_i t) \exp(-\lambda_i t) + \frac{1}{3}, \]  

where \( f_i \) and \( \lambda_i \) are the muon precession frequency and its exponential relaxation rate, respectively, at the \( i \)th site \((f_i < f_{i+1})\). Here, \( f_i \) is converted into \( H_{\text{int,i}} \) by \( f_i = 13.553 \) kHz/Oe \( \times H_{\text{int,i}} \). When \( \lambda_i = 0 \), we obtain the ZF spectrum without relaxation, as seen in Fig. 8(b). Then, the calculated ZF spectrum was fitted by Eq. (2). As seen in Table I, such fit reproduces a delay and progress of \( \phi_i \), obtained by the fit for the measured spectrum at 1.7 K. This clearly demonstrates that the delay and progress of \( \phi_i \) are caused by a wide field distribution and also confirms the reliability of the proposed AF spin structure and the dipole field calculations. Moreover, since the fit by Eq. (2) with \( \phi_i = 0 \) yields a very similar result to that obtained by Eq. (2), the result of the global fit is acceptable.

Even for the calculated spectrum without a relaxation, the fit using Eq. (2) provides that \( \lambda_{\text{AF1}} = (38 \pm 9) \times 10^6 \) s\(^{-1}\) and \( \lambda_{\text{AF2}} = (1 \pm 2) \times 10^6 \) s\(^{-1}\). Since we measured a powder sample, a random distribution of \( H_{\text{int}} \) together with an imperfection of the crystalline solid naturally induce an additional relaxation. Also, even for single crystal samples, the ordered
The calculated $f_i$ is proportional to the AF ordered moment ($\mu_{\text{ord}}$) of the Cr ions. Since $\mu_{\text{ord}}$ is reported to be 2.7 $\mu_B$ at 9 K for the double-$Q$ 120° structure by the neutron experiment,\textsuperscript{12} we used $\mu_{\text{ord}}=2.7 \mu_B$ for the present dipole field calculations. Figure 8 shows that the calculated spectrum roughly reproduces the measured ZF spectrum if we ignore damping. More correctly, based on the fit result of $f_{\text{AF,ij}}$ in Table I, $\mu_{\text{ord}}$ is estimated as 2.4 $\pm$ 0.1 $\mu_B$ from the present $\mu^*\text{SR}$ measurements, being consistent with the neutron results.

Taking into account the nuclear magnetic moments of $^7\text{Li}$, $^6\text{Li}$, and $^{53}\text{Cr}$, the same dipole field calculations in the paramagnetic state provided that $\Delta^{\text{PM}}_\text{calc}=(0.485 \pm 0.002) \times 10^6$ s$^{-1}$. This is roughly in agreement with the experimental result, although the calculated $\Delta^{\text{PM}}_\text{calc}$ is 55% larger [see Fig. 7(b)] than the measured $\Delta^{\text{meas}}_\text{meas}=(0.3124 \pm 0.0001) \times 10^6$ s$^{-1}$. Consequently, the muon sites, 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.

B. Possible origin of the anomaly around 115 K

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. 7(b)], the change at $T_c$ is most likely due to a diffusive motion of the Li$^+$ ions. This is because the relationship between $\nu$ and $T$ is expected to be given by $\nu=\exp(-1/T)$ for Li diffusion.\textsuperscript{31} 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., $\text{Cr}^{3+} \leftrightarrow \text{Cr}^{4+}\delta+\text{Cr}^{2+}\delta$, as in the case for Na$_{0.5}$CoO$_2$.$^32,33$ However, even for the mixed valence state of the Co ions in Na$_{0.5}$CoO$_2$, $\delta$ was reported below 0.2.$^{32,33}$ Hence, it would be very difficult to detect $\delta$ for LiCrO$_2$, even if such charge disproportionation occurs. Actually, although we attempted to fit the ZF spectrum by $G^{\text{DGKT}}(\Delta, \nu, t) \exp(-\nu_{\text{Cr}}, t)$, where the exponential relaxation should corre-

![Image](image_url)

**FIG. 8.** (Color online) (a) Field distribution for LiCrO$_2$ predicted from dipole field calculations (vertical bars) using the spin structure from Ref. 12, (b) calculated ZF-$\mu^*$SR time spectrum (thick solid line) and the fit curve using Eq. (2) (thin solid line) and Eq. (2) with $\phi=0$ (thin broken line), and (c) measured ZF-$\mu^*$SR time spectrum at 1.7 K. In the calculations, we used $\mu_{\text{ord}}=2.7 \mu_B$, where $\mu_{\text{ord}}$ is the magnitude of the ordered moment of the Cr ions estimated by neutron measurements (Ref. 12). The calculated ZF spectrum was obtained by Eq. (4) with $\lambda_c=0$.

Spin lattice is not perfect to the implanted muons causing a nonzero relaxation rate in the ZF spectrum.\textsuperscript{29} We wish to note that the prediction for the magnitude of $\lambda_{\text{AF,ij}}$ (i.e., $\lambda_{\text{AF,1}}>\lambda_{\text{AF,2}}$) is consistent with the fit result for the ZF spectrum measured at 1.7 K.

<p>| Table I. Fit parameters obtained by Eq. (2) for the calculated and measured spectrum. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Calculated spectrum</th>
<th>$A_{\text{AF,1}}/A_{\text{AF,2}}$</th>
<th>$f_{\text{AF,1}}$ (MHz)</th>
<th>$f_{\text{AF,2}}$ (MHz)</th>
<th>$\lambda_{\text{AF,1}}$ (10$^6$ s$^{-1}$)</th>
<th>$\lambda_{\text{AF,2}}$ (10$^6$ s$^{-1}$)</th>
<th>$\phi_1$ (deg)</th>
<th>$\phi_2$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation (2)</td>
<td>2.4 $\pm$ 1.0</td>
<td>25.8 $\pm$ 1.3</td>
<td>45.1 $\pm$ 0.3</td>
<td>38 $\pm$ 9</td>
<td>1 $\pm$ 2</td>
<td>44.4 $\pm$ 0.2</td>
<td>$-49.9 \pm$ 0.2</td>
</tr>
<tr>
<td>Equation (2) with $\phi=0$</td>
<td>1.7 $\pm$ 0.7</td>
<td>27.8 $\pm$ 0.9</td>
<td>45.7 $\pm$ 0.2</td>
<td>31 $\pm$ 8</td>
<td>1 $\pm$ 2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Measured spectrum at 1.7 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equation (2)</td>
<td>1.16 $\pm$ 0.05</td>
<td>17.3 $\pm$ 0.9</td>
<td>45.8 $\pm$ 0.6</td>
<td>52 $\pm$ 4</td>
<td>34 $\pm$ 2</td>
<td>48 $\pm$ 7</td>
<td>$-52 \pm$ 7</td>
</tr>
<tr>
<td>Equation (2) with $\phi=0$</td>
<td>1.48 $\pm$ 0.07</td>
<td>24.3 $\pm$ 0.6</td>
<td>41.9 $\pm$ 0.3</td>
<td>52 $\pm$ 3</td>
<td>30 $\pm$ 2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
spond to the fluctuation of the Cr spins, the $\chi(T)$ curve exhibits no crucial anomaly around $T_N$. It should also be noted that a Kubo-Toyabe function is only an approximation of the nuclear dipole contribution to the ZF-$\mu^+\text{SR}$ spectrum. Hence, although the spectrum is well fitted by a Kubo-Toyabe function, there is still a possibility that the dynamics of the Li ions for the magnetic nature of LiCrO$_2$ is observed by neutron measurements down to the low-est $T$ measured, a long-range AF order is clearly detected in LiCrO$_2$ by neutron measurements, for reasons currently unknown. As in the case for Na$_{0.5}$CoO$_2$ and K$_{0.5}$CoO$_2$ 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 $T \approx 62.5$ 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 magnetic contribution by only subtracting $C_p$ for LiCoO$_2$ from $C_p$ for LiCrO$_2$, as in the case for Na$_{0.5}$CoO$_2$.

V. CONCLUSIONS

By means of a positive muon-spin rotation and relaxation ($\mu^+\text{SR}$) 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, ZF-$\mu^+\text{SR}$ 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-$\mu^+\text{SR}$ measurements clearly indicated the absence of magnetic order for $T \approx 62.5$ 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.

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8 e0589@mosk.tytlabs.co.jp
9 Present address: Muon Science Laboratory, Institute of Materials Structure Science, KEK, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan.
