Internal magnetic field in the zigzag-chain family 
(Na,Ca)Cr$_2$O$_4$

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Abstract. In order to elucidate the magnetic nature for a novel one-dimensional zigzag chain compound, NaCr$_2$O$_4$, we have measured $\mu^+\text{SR}$ spectra using a powder sample in the temperature range between 2 and 200 K. Weak transverse field (wTF-) $\mu^+\text{SR}$ measurements indicated that the whole volume of the sample enters into an antiferromagnetic (AF) phase below $T_N = 125$ K. The zero field (ZF-) $\mu^+\text{SR}$ spectrum obtained below $T_N$ exhibits a clear oscillation with a single muon-spin precession frequency ($f_\mu$). This suggests that static AF order is formed below $T_N$ and that all the implanted muons sense the same internal magnetic field. The temperature dependence of $f_\mu$ was found to be very similar to that for the intensity of the magnetic Bragg peak in neutron diffraction (ND) measurements. On the other hand, the ZF-$\mu^+\text{SR}$ spectrum for the isostructural compound, $\beta$-CaCr$_2$O$_4$, showed a rapidly damped oscillation below $T_N = 21$ K, supporting the formation of incommensurate AF order, as proposed by ND.

1. Introduction

The magnetic interaction on triangular crystal lattices is often frustrated in the sense that not all pair-wise interactions are satisfied. Such frustration leads to unconventional ground states, such as glassy, spin-ice and spin-liquid-like states. Among such frustrated systems, one-dimensional systems offer a typical showcase that relatively simple systems display glamorous magnetic phenomena [1, 2] and complex phases [3, 4, 5, 6, 7]. This is mainly due to the competition between nearest-neighbor (intra-chain) and next-nearest-neighbor (inter-chain) interactions. Following progress in the development of sample synthesis techniques, particularly synthesis under high-pressures, many novel geometrically frustrated materials have been found, resulting in a new dawn for the research of this field.

In order to identify the magnetic nature of several one-dimensional (1D) systems, we have previously studied with $\mu^+\text{SR}$ the Na$_x$Ca$_{1-x}$V$_2$O$_4$ family [8, 9, 10], the AMn$_2$O$_4$ with $A = $Li, Na, [11] the EuL$_2$O$_4$ where $L = $Eu, Gd, Yb, Lu [12], and the A$_2$Cr$_8$O$_{16}$ with $A = $K, Rb [13]. Following upon these experiments, we have started a $\mu^+\text{SR}$ experiment on the new 1D zigzag-chain family Na$_x$Ca$_{1-x}$Cr$_2$O$_4$ [14], which is a solid solution system between $\beta$-CaCr$_2$O$_4$ [15, 16].

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and novel NaCr$_2$O$_4$ [17]. Both compounds possess a CaFe$_2$O$_4$ (CFO)-type $Pnma$ structure and the goal in this experiment is to clarify the magnetic ground state of NaCr$_2$O$_4$ and to determine the magnetic phase diagram as a function of Ca content. Here, we report the $\mu^+$SR result on NaCr$_2$O$_4$ and $\beta$-CaCr$_2$O$_4$, and compare it with the result obtained by neutron diffraction (ND) measurements.

2. Experimental

A polycrystalline sample of NaCr$_2$O$_4$ was synthesized under 7 GPa at 1573 K for 12 h. A stoichiometric mixture of NaCrO$_2$, Cr$_2$O$_3$, and CrO$_3$ was mixed and sealed in a gold capsule in a glove box filled with Ar gas. Then, the mixture was pressed in a belt-type press and then heated for 12 h. NaCrO$_2$ was prepared by firing a stoichiometric mixture of Na$_2$CO$_3$ and Cr$_2$O$_3$ at 1123 K for 15 h in a flowing Ar gas.

A polycrystalline sample of $\beta$-CaCr$_2$O$_4$ was synthesized by a conventional solid-state reaction under ambient pressure. The stoichiometric mixture of CaCO$_3$ and Cr$_2$O$_3$ was fired twice in an Ar gas flow at 1573 K for $\sim$12 h with an intermediate regrinding.

The details of the synthesis were described elsewhere [14]. A powder x-ray diffraction (XRD) analysis showed that the sample was almost single phase with an orthorhombic system of space group $Pnma$ at ambient $T$, but contains a small amount of Cr$_2$O$_3$ (less than 2 wt%). Magnetization measurements using a SQUID magnetometer indicated the presence of antiferromagnetic transition at 125 K ($= T_N$). The $\mu^+$SR measurements were performed on the M20 surface muon beam line at TRIUMF.
3. Results and discussion

3.1. NaCr$_2$O$_4$

**Figure 3.** $T$ dependences of (a) the muon-spin precession frequency ($f_{\mu}$) and (b) the weak transverse field asymmetry ($A_{TF}$) for NaCr$_2$O$_4$. The data in (a) were obtained by fitting the ZF-$\mu$SR spectrum with eq. (1), while the data in (b) were estimated by fitting the wTF-$\mu$SR spectrum with $A_0P_{TF}(t) = A_{TF} \cos(2\pi f_{TF} + \phi_{TF}) \exp(-\lambda_{TF}t)$. In (a), the normalized structure factor for the magnetic Bragg peak 001 extracted from the neutron diffraction data [19] is also plotted for comparison.

Figure 1 shows the variation of the ZF-$\mu$SR time-spectrum with $T$ for NaCr$_2$O$_4$. The spectra obtained below $T_N$ exhibit a damped oscillation, which demonstrates the formation of static magnetic order. Note that there are four oscillatory signals in the ZF-spectrum below 120 K for the isostructural compound NaV$_2$O$_4$, due to the presence of four different muon sites in the lattice [8, 10]. In order to confirm the existence or absence of multiple oscillatory signals in the ZF-spectrum, Fig. 2 shows the $T$ dependence of the Fourier transform frequency-spectra of the ZF-$\mu$SR time-spectra. It is clearly seen that there is only one signal with a wide frequency distribution. This is consistent with the damped oscillatory signal in the time-spectrum (Fig. 1). Furthermore, the full width at half maximum of the peak appears roughly $T$-independent, while the frequency of the oscillatory signal depends on $T$. This provides a clue to understand the origin of the wide distribution of the internal magnetic field ($H_{int}$) in the NaCr$_2$O$_4$ lattice. The amplitude of the oscillatory signal of the ZF-$\mu$SR spectrum at 2 K is smaller by $\sim 10\%$ than that at 110 K (see Fig. 1). In fact, as $T$ decreases from $T_N$, the peak

**Figure 4.** Powder neutron diffraction patterns obtained at (a) 140 K and (b) 1.6 K for NaCr$_2$O$_4$ [19]. In (b), only the magnetic Bragg peaks are indexed, while the nuclear Bragg peaks are indexed in (a).
Figure 5. The ZF-μ+SR time-spectrum for β-CaCrO₄ obtained at 2 K. A solid line represents the best fit using an exponentially relaxing Bessel function \[ J(2\pi f_{\mu} t) \].

The height of the Fourier power spectrum decreases, while the peak width increases (see Fig. 2). This suggests that there are additional oscillatory signals at low T due to the existence of the multiple muon sites. However, since it is difficult to fit the ZF-μ+SR spectra with multiple oscillatory signals, we tentatively fitted the spectrum by a combination of an exponentially relaxing cosine signal and a slowly relaxing non-oscillatory signal based on the above Fourier transform result. The former corresponds to the muon-spin precession signal due to \( H_{\text{int}} \), while the latter is the “1/3 tail” signal for a powder sample in an ordered state.

The expression for the fit function is:

\[
A_0 P_{ZF}(t) = A_{AF} \cos(2\pi f_{\mu} t + \phi) \exp(-\lambda_{AF} t) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t),
\]

where \( A_0 \) is the initial asymmetry at \( t = 0 \), \( f_{\mu} \) is the muon-spin precession frequency, \( \phi \) is the initial phase of the precession, \( A_{AF} \) and \( A_{\text{tail}} \) are the asymmetries for the two signals, and \( \lambda_{AF} \) and \( \lambda_{\text{tail}} \) are their exponential relaxation rates.

Figure 3 shows the \( T \) dependences of (a) \( f_{\mu} \) and (b) the normalized wTF asymmetry \( [A_{TF}(T)/A_0] \) obtained with \( H_{TF} = 50 \text{ Oe} \) in order to check the volume fraction of nonmagnetic phase(s) in the sample. The \( f_{\mu}(T) \) curve shows an order-parameter-like \( T \) dependence. In (a), the normalized magnetic moment \( \sqrt{I_{\text{ND}}(T)/I_{\text{ND}}(T \to 0 \text{ K})} \) derived from the intensity of the magnetic Bragg peak \( I_{\text{ND}}(T) \) is also shown as a function of \( T \). The two \( T \) dependences are almost identical each other, as expected. The \( A_{TF}(T)/A_0 \) curve shows a step-like change between 0 and 1 at \( T_N \), suggesting the whole volume of the sample enters into a magnetic ordered state within the wTF-μ+SR resolution (around a few %). This is also consistent with the result of the XRD analysis that suggests the volume of impurity phase is below 2%.

Prior to the μ+SR result of CaCrO₄, we briefly explain the result of powder ND measurements on NaCrO₄ [19]. Figure 4 shows the powder ND pattern obtained at 1.6 and 140 K. Several magnetic Bragg peaks are clearly seen at 1.7 K and they are well indexed by the magnetic structure with \( \vec{k} = (1,0,1) \), where \( \vec{k} \) is the propagation vector. Our preliminary Rietveld analysis on the ND pattern suggested that the magnetic moments of the Cr ions aligns ferromagnetically along the \( b \)-axis, but antiferromagnetically along the \( a \)-axis. Although the Cr moments are proposed to be canted in the \( ac \)-plane [20], it is very difficult to determine the canted AF structure based only on the powder ND pattern.
3.2. β-CaCr$_2$O$_4$

Although the $T$ dependence of wTF-$\mu^+$SR parameters for β-CaCr$_2$O$_4$ with $T_N = 21$ K were studied with a pulsed muon beam together with ND [16], the microscopic magnetic nature was not fully clarified due to the limited time resolution of the pulsed muon beam.

Figure 5 shows the ZF-$\mu^+$SR spectrum for β-CaCr$_2$O$_4$ obtained at the lowest $T$ measured. One can clearly see a rapidly damped oscillation due to an inhomogeneous distribution of $H_{int}$, although static magnetic order is formed. When we fitted the ZF-spectrum with eq. (1) as for NaCr$_2$O$_4$, such fit provided that $\phi = -38.55^\circ$. This suggests the formation of incommensurate (IC) magnetic order [18], which is consistent with the ND result [16]. In fact, the ZF-spectrum was well fitted by a zeroth-order Bessel function of the first kind [$J(2\pi f_{AF} t)$], which is usually used for IC magnetic order [18, 21, 22].

Therefore, for the solid solution system, Na$_x$Ca$_{1-x}$Cr$_2$O$_4$, it is expected that IC order changes into commensurate order with $x$. This means the existence of a magnetic lock-in transition at a certain $x$. In order to clarify the magnetic phase diagram of Na$_x$Ca$_{1-x}$Cr$_2$O$_4$, further $\mu^+$SR study is in progress.

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