The magnetic phase of the perovskite \( \text{CaCrO}_3 \) studied with \( \mu^+ \text{SR} \)

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(Dated: April 29, 2010)

We investigated the magnetic phase of the perovskite \( \text{CaCrO}_3 \) by using the muon spin relaxation technique accompanied by susceptibility measurements. A thermal hysteresis loop is identified with a width of about 1 K at the transition temperature. Within the time scale of the muon lifetime, a static antiferromagnetic order is revealed with distinct multiple internal fields which are experienced in the muon interstitial sites below the phase-transition temperature, \( T_N = 90 \text{ K} \). Above \( T_N \), lattice deformations are indicated by transverse-field muon-spin rotation and relaxation suggesting a magneto-elastic mechanism.

I. INTRODUCTION

The co-existence of metallic conductivity and antiferromagnetism is uncommon and has therefore inspired theoretical \(^1\) and experimental \(^2,3\) interests, particularly for transition metal oxides (\( \text{MO}_2 \)), due to a strong hybridization of \( d \) orbital of the metal ion (\( M \)) and \( 2p \) orbital of the oxygen (\( O \)). The magnetic properties in these systems are governed mainly by a super-exchange interaction via an oxygen between the nearest neighboring (NN) \( M \) ions, and additionally by a competition between the NN interaction and the next-nearest-neighbor interaction. This competition has been reported to cause the magnetic order and affect the structural and electronic properties. In most experimental systems \(^4,5\), these interactions are characterized by low dimensionality thereby granting the exotic coexistence of the antiferromagnetic (AFM) order and metallic conductivity. The three-dimensional perovskite \( \text{CaCrO}_3 \) represent an exception.

Although \( \text{CaCrO}_3 \) was reported to show semiconducting \(^6\) or insulating \(^2\) properties with AFM order below 90 K (\( = T_N \)), recent measurements on single crystals, grown in high-pressure synthesis, indicated metallic conductivity for \( \text{CaCrO}_3 \) even below \( T_N \).\(^7\) This was also supported by infrared reflectivity measurements on a polycrystalline sample.\(^8\) Furthermore, based on powder neutron diffraction analysis, the AFM spin structure was proposed as a \( C \)-type AFM, in which Cr spins order antiferromagnetically in the \( ab \) plane, but ferromagnetically along the \( c \) axis.\(^9\) A high-temperature Curie-Weiss fit of the susceptibility-versus-\( T \) curve in the \( T \) range between 400 and 600 K indicated the effective magnetic moment (\( \mu_{\text{eff}} \)) of Cr to be 3.6 \( \mu_B \) and the Weiss \( T \) (\( \Theta_W \)) is about -920 K.\(^8\)\(^8\) Since the Cr ions are in a 4+ state with \( S=1 \), the obtained \( \mu_{\text{eff}} \) is rather high compared with the localized-spin-only value (2.85 \( \mu_B \)). Moreover, it was found that the \( \text{CaCrO}_3 \) system has a magneto-elastic distortion driven by the Cr moments,\(^8\) resulting in a small change in the orthorhombic lattice parameters at \( T_N \). Despite the several macroscopic measurements mentioned above, the microscopic magnetic nature of \( \text{CaCrO}_3 \) has not been investigated so far, because of the difficulty of sample preparation and eventually the absence of NMR-active elements in \( \text{CaCrO}_3 \), as the natural abundance for the NMR-active \( ^{43}\text{Ca} \) is 0.14% and that for \( ^{53}\text{Cr} \) is 9.5%.

In contrast to NMR, the muon-spin rotation and relaxation (\( \mu^+\text{SR} \)) technique is applicable to all magnetic materials \(^9,10\), even if they lack elements with nuclear magnetic moments. We have, therefore, carried out an experimental study on the perovskite \( \text{CaCrO}_3 \) (see Fig. 1) by means of \( \mu^+\text{SR} \) due to its remarkable ability in detecting local magnetic order, whether it is short- or long-ranged. Combining bulk dc-susceptibility and \( \mu^+\text{SR} \) measurements, we characterize the magnetic properties of \( \text{CaCrO}_3 \). Our major finding is a \( C \)-type AFM phase, determined from the multiple frequencies revealed in zero-field (ZF) \( \mu^+\text{SR} \). Such frequencies are the attributes of the several \( \mu^+ \) interstitial sites in the AFM phase. Second, the transverse-field (TF) \( \mu^+\text{SR} \) signals also suggests a deformation of the lattice, thereby corroborating that \( \text{CaCrO}_3 \) experiences a magneto-elastic distortion.
The GdFeO$_3$-type crystal structure (space group Pbnm, No. 62) of CaCrO$_3$ that evolves from the ideal perovskite structure by a rotation ($\Phi \approx 8.2^\circ$) and tilt ($\Theta \approx 10.5^\circ$) of the CrO$_6$ octahedra [3]. Thin purple (light grey) lines enclose the unit cell.

II. EXPERIMENT

Polycrystalline CaCrO$_3$ was prepared by a solid state reaction of CaO and CrO$_3$ under 4 GPa at 1000$^\circ$C for 30 min in the Institute of Solid State Physics of University of Tokyo. dc-$\chi$ measurement (shown later) and powder diffraction were performed and agreed with previously published data. In the $\mu^+$SR experiment, the powder sample was placed in a small envelope made of very thin Al-coated Mylar tape and attached to a low-background sample holder. In order to make certain that the muon stopped primarily inside the sample, we ensured that the side facing the muon beamline was only covered by a single layer of the mylar tape. Subsequently, ZF, TF and longitudinal-field (LF) $\mu^+$SR spectra were collected for $1.8 \text{ K} \leq T \leq 150 \text{ K}$, at the M20 and M15 surface muon channel at TRIUMF, Vancouver, Canada. The experimental setup and techniques are described in detail elsewhere [11].

III. RESULTS

The bulk magnetization and susceptibility of CaCrO$_3$ is shown in Fig. 2 as a function of $T$ and $H$. The temperature dependence of the bulk dc susceptibility, $\chi$, was measured using a commercial superconducting quantum interference device magnetometer (Magnetic Property Measurement System - Quantum Design). The magnetic transition is seen clearly at $T_N \sim 90 \text{ K}$, however the $\chi(T)$ curve shows the appearance of small spontaneous magnetization below $T_N$, that is not of a typical AFM transition. The same $\chi(T)$ behavior is seen at all fields measured (1 kOe $\leq H \leq 50 \text{ kOe}$, not shown), therefore this can be ruled-out as field-induced. Figure 2(a) displays the characteristic $\chi(T)$ curves obtained on cooling and heating with $H = 50 \text{ kOe}$ in FC mode. (b) The normalized wTF Asymmetry with applied field $H = 30 \text{ Oe}$. (c) The magnetization ($M$) versus $H$ at 90 (black line), 80 (blue), and 5 K (red).

To corroborate this magnetic transition, we performed weak transverse-field measurements. A weak transverse-field (wTF) measurements, where the field applied is perpendicular to the muon spin direction and is weak compared to any spontaneous internal fields in the ordered phase, is a sensitive probe to local magnetic order. In Fig. 2(b), we plot the $T$ dependence of the normalized wTF asymmetry ($NA_{\text{wTF}}$) taken at 30 Oe on heating. Note that the $NA_{\text{wTF}}$ is proportional to the volume fraction of the paramagnetic phase. The magnetic phase transition, as indicated by the wTF measurements, also identifies the transition at $T_N = 90 \text{ K}$. To further explore the magnetic phase we...
performed ZF $\mu^+\text{SR}$, which is a site-sensitive probe in which the muon asymmetry is only affected by the internal magnetic fields.

ZF $\mu^+\text{SR}$ measurements were taken in the same configuration as described in Sec. II. The inset of Fig. 3(a) shows the raw ZF Asymmetry spectrum. (b) The temperature dependence of the muon precession frequencies at the AFM phase.

In order to study the magneto-elastic coupling, TF $\mu^+\text{SR}$ measurements were taken at fields ranging from 2 to 50 kOe at the transition temperature. The inset of Fig. 4 plots the muon decay asymmetry in a transverse field of 2 kOe rotated at a reference frame of 26.5 MHz. Since a high magnetic field is available only along the axial direction, TF measurements were performed in a spin-rotated mode, where the muon spin is rotated 90° thereby perpendicular to the field direction. The LF measurements, were performed in a non-spin-rotated mode, therefore the spin and the field were parallel. No temperature dependence was found on the muon relaxation in the LF measurements, and was at least an order of magnitude smaller than the TF relaxation. It should be noted that TF measurements probe both the static and dynamic field fluctuations and the LF measurements probes the dynamic fluctuations only. Hence, it was found that the dynamic fluctuations are weak compared to the static fluctuations, therefore negligible.

FIG. 3: (Color online) (a) The Fourier Transform of the Zero Field spectra at $T = 40$ K. Inset shows the raw ZF Asymmetry spectrum. (b) The temperature dependence of the muon precession frequencies at the AFM phase.
depends on the muon-electron distance and is isotropic, the neighboring electron. We assume that the coupling

\[ A \propto \rho \] 

is the solid line in the plot. Figure 4 depicts the magnetization, \( M \). At \( M \approx 0.06 \text{ emu/mol} \), \( R_{TF} \) increases more rapidly with \( R \) than for \( 90 \text{ K} \), not shown) of \( \sigma \), using Eq. (2), we can calculate \( \Delta \sigma / \sigma \), where \( \Delta \sigma \) and \( \sigma \) are the standard deviation and average of \( \sigma \) respectively. The ratio \( \Delta \sigma / \sigma \) gives a measure of the relative change in the variation of the muon-electron distance due to temperature changes. We find that \( \Delta \sigma / \sigma \) is \( \sim 208\% \), for comparison, compounds which do not distort have a much smaller \( \Delta \sigma / \sigma \). For example, the pyrochlore \( \text{Tb}_2\text{Ti}_2\text{O}_7 \) has \( \Delta \sigma / \sigma \) of 15\% \([12]\). A possible reason for such a distortion is a response of the lattice to the magnetic interactions through a magneto-elastic coupling \([12] \). Such coupling relieves the frustrated Cr interactions by causing lattice deformations. This is consistent with the scenario suggested by neutron scattering studies \([2]\).

![Diagram](image.png)

**FIG. 4**: (Color online) The TF Relaxation rate, \( R_{TF} \) versus the magnetization, \( M \). Inset, the muon decay asymmetry in Transverse Field of 2 kOe, rotated in a reference frame of 26.5 MHz.

The TF muon-spin polarization is best described by

\[ A_0 P_{TF} = A_0 \exp(-R_{TF}t) \cos(\omega t + \varphi) \]  

where \( R_{TF} = (T_2^*)^{-1} \) is the TF relaxation rate and \( \omega = \gamma \mu H_{TF} \). The quality of the fit is described by the solid line in the plot. This suggests a modification in the hyperfine coupling, which induces the abrupt change in the lattice deformations. This is consistent with the scenario suggested by neutron scattering studies \([2]\).

IV. SUMMARY

By means of \( \mu^+\)SR and susceptibility, we clarified the nature of the magnetic phase of the perovskite \( \text{CaCrO}_3 \) below \( T_N \). Susceptibility measurements demonstrate a presence of a weak ferromagnetic contribution in the magnetic hysteresis loops. However, \( \mu^+\)SR demonstrates the formation of static AFM order below \( T_N \). Based on electrostatic and dipole field calculations, the \( C_3 \)-AFM structure, which was proposed by neutron measurements, is found to be the most reasonable in explaining the internal magnetic fields detected by zero-field \( \mu^+\)SR measurements.

Transverse-field \( \mu^+\)SR measurements in the paramagnetic phase provided the temperature dependence of the spin-spin relaxation rate \( (T_2^{-1}) \). The lack of a linear relationship between \( T_2^{-1} \) and magnetization above the vicinity of \( T_N \) suggests the presence of magneto-elastic coupling, which induces the abrupt change in the lattice parameters at \( T_N \), and reduce the frustrated interactions.

Although the overall \( \mu^+\)SR results confirm the past neutron results, it should be noted that the time window and spatial resolution of \( \mu^+\)SR are different from those of neutron scattering. Therefore, combining the past neutron results, the magnetic and structural nature of \( \text{CaCrO}_3 \) have been fully elucidated by this work.

Acknowledgments

We are grateful to the staff of TRIUMF for assistance with the \( \mu^+\)SR experiments. JHB is supported at UBC by CIFAR, NSERC of Canada, and (through TRIUMF) by NRC of Canada and KHC by NSERC of Canada and (through TRIUMF) by NRC of Canada. This work is also supported by Grant-in-Aid for Scientific Research (B), 19340107, MEXT, Japan.

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