

**I. INTRODUCTION**

Disilver transition-metal dioxides, Ag₂MO₂ with \( M = \text{Ni and Mn} \), which consist of alternating stacks of [Ag₂]⁻¹ and [MO₂]⁻¹ planes,¹⁻³ have attracted a special attention due to the coexistence of metallic conductivity and antiferromagnetic (AF) order on a two-dimensional triangular lattice of M ions. Although the [Ag₂] plane is thought to be responsible for the metallic conductivity, recent soft x-ray photoemission and absorption spectroscopy measurements on Ag₂NiO₂ and Ag₂MnO₂ revealed a contribution from the 3d electrons of Ni and Mn on the density of states at the Fermi level \( (E_F) \).² This is consistent with the mass enhancement of carriers below \( T_N \).² Furthermore, such hybridized Ni and Mn 3d states at \( E_F \) would enhance the magnetic correlations between the adjacent MO₂ planes through the superexchange interaction via an \( M\text{-O}-(\text{Ag}_2)\text{-O-M} \) pathway.

Indeed, a very recent neutron diffraction (ND) experiment on Ag₂NiO₂⁵ clarified that the magnetic structure is a modulated A-type AF, in which Ni spins align antiparallel along the c-axis through the [Ag₂] plane. The muon sensitivity to the \( \mu^+ \)SR experiments on a polycrystalline Ag₂CrO₂ sample at temperatures between 1.8 and 40 K by combining the \( \mu^+ \)SR result with the prediction for muon sites in the lattice from first principles calculations, a partially disordered AF state was found to be the most reasonable spin structure for Ag₂CrO₂. A sudden decrease of the electrical resistivity at \( T_N \) suggests a strong hybridization of Cr 3d with Ag 5s orbital,⁶ as found for Ag₂NiO₂.⁴ The presence of long-range AF order is, hence, expected through the 3D interaction via the Cr-O-(Ag₂)-O-Cr pathways. In fact, several magnetic Bragg peaks were observed below \( T_N \) by ND⁶ and the proposed magnetic structure was a partial disordered AF (PDA) state with \( 5 \times 5 \) unit cells in the \( ab \) plane.

The PDA state was already reported to appear in the Ising chain systems, such as Ca₃Co₂O₆¹¹ and Ca₃CoRhO₆.¹² The \( \mu^+ \)SR spectrum for these compounds under zero magnetic field (ZF) exhibits a very rapidly damped oscillation¹³⁻¹⁵ due to a wide distribution of the internal magnetic field \( (H_{int}) \) at the muon site(s). \( \mu^+ \)SR is particularly sensitive to the local magnetic environment, since the \( \mu^+ \)SR result with the prediction for muon sites in the lattice from first principles calculations, we conjecture the AF magnetic structure below \( T_N \). Finally, we attempt to solve the discrepancy between ND⁵ and \( \mu^+ \)SR⁶ results for the AF structure in Ag₂NiO₂ using the information on the muon site for Ag₂CrO₂.

**II. EXPERIMENTAL**

A powder Ag₂CrO₂ sample was prepared at the National Institute for Materials Science (NIMS) by a solid-state reaction technique using reagent grade Ag, Ag₂O, and Cr₂O₃ powders as starting materials. The mixture was encapsulated into a gold capsule, and then heated at 1200 °C for 1 h under 6 GPa using a flat-belt-type high-pressure apparatus. According to powder x-ray diffraction (XRD) analysis at ambient temperature,
the sample was single phase of trigonal symmetry with space group $P 3m 1$. The structural and physical properties of Ag$_2$CrO$_2$ are reported in Refs. 9 and 10.

The temperature dependence of the magnetic susceptibility ($\chi = M/H$, where $M$ is magnetization) was measured below 400 K under a $H \leq 10$ kOe field using a SQUID magnetometer (MPMS, Quantum Design). (Fig. 1) The temperature independent susceptibility ($\chi_0 = 0.0021 \pm 0.0004$ emu/mol), Weiss temperature ($\Theta_{CW} = -80 \pm 4$ K), and effective magnetic moment ($\mu_{eff} = 3.39 \pm 0.03 \mu_B$) were extracted from the $\chi(T)$ curve by fitting to a Curie-Weiss law, $\chi = \chi_0 + C / (T - \Theta_{CW})$ and $C = (N \mu_B^2/3 k_B) \mu_{eff}^2$ in the $T$ range between 200 and 400 K. Here, $N$ is the number density of Cr spins, $g$ is the Landé $g$ factor, $\mu_B$ is the Bohr magneton, and $k_B$ is Boltzmann’s constant. The obtained values are consistent with those from literature.

The $\mu^+ \text{SR}$ spectra were recorded at a surface muon beam line using the GPS spectrometer of PSI in Switzerland. Approximately 500 mg of powder sample were placed in an envelope with $1 \times 1$ cm$^2$ area, made of Al-coated Mylar tape with 0.05-mm thickness in order to minimize the signal from the envelope. The envelope was attached to a low-background sample holder in a liquid-He flow-type cryostat for measurements in the $T$ range between 2 and 40 K. The experimental techniques are described in more detail elsewhere.

III. $\mu^+ \text{SR TECHNIQUE}^{18}$

When spin-polarized muons are implanted into a magnetically ordered material in ZF, the muon-spins precess around the local magnetic fields $H_{int}$ in the material at the frequency, $f = (\gamma_\mu / 2\pi) H_{int}$, where $\gamma_\mu / 2\pi = 13.554$ kHz/Oe is the muon gyromagnetic ratio. Such oscillation in the ZF spectrum is represented by

$$A_0 P_{ZF}(t) = A_0 \left[ \frac{1}{3} G_s(t) \cos(2\pi f t + \phi) + \frac{1}{3} G_z(t) \right].$$

Here, $A_0$ is the initial asymmetry, which depends on many factors such as the muon decay anisotropy, the solid angle subtended by the detector, its overall detection efficiency, positron absorption in the sample and its surroundings, etc. For a typical experiment and detector, $A_0$ ranges between 0.2 and 0.4. More correctly, for the present experiment, $A_0 = 0.24$ from the measurements of a silver reference. $P_{ZF}(t)$ is the muon spin polarization function under ZF.

Both $G_s(t)$ and $G_z(t)$ are the relaxation function caused by inhomogeneous distribution of $H_{int}$ at the muon sites.

When there are multiple muon sites with different $H_{int}$, the ZF spectrum is given by

$$A_0 P_{ZF}(t) = \sum_{i=1}^{n} A_i \left[ \frac{2}{3} G_s^{(i)}(t) \cos(2\pi f t + \phi_i) + \frac{1}{3} G_z^{(i)}(t) \right],$$

where $n$ is the number of the muon sites and $\sum_{i=1}^{n} A_i = A_0$. If such multiple muon sites are caused by the coexistence of multiple phases in the sample, $A_i/A_0$ corresponds to the volume fraction of the $i$th phase. On the other hand, if all the muon sites are crystallographically equivalent but magnetically different, $A_i/A_0$ shows the fraction of the muon sites with $H_{int}^{(i)}$ to the all sites.

IV. RESULTS

A. Below $T_N$

Figure 2(a) shows the ZF-$\mu^+ \text{SR}$ time spectra for Ag$_2$CrO$_2$ recorded at temperatures between 1.8 and 24 K. A clear oscillatory signal is observed below 24 K at $T = T_N$, although the ZF spectrum is strongly damped even at 1.8 K. This suggests the formation of a static but inhomogeneous internal field at the muon site(s) below 24 K. In addition, the muon-spin precession frequency increases very slightly with decreasing $T$, and looks roughly $T$-independent for $T \leq 22$ K. Making comparison with the ZF spectrum for Ag$_2$NiO$_2$ and Ag$_2$MnO$_2$ obtained at the lowest $T$ measured [see Fig. 2(b)], the AF spin structure for Ag$_2$CrO$_2$ is likely to be similar to that for Ag$_2$NiO$_2$.

The ZF spectra for Ag$_2$CrO$_2$ are well fitted by a combination of an exponentially relaxing cosine oscillation for the static $H_{int}$ caused by the formation of AF order and two exponentially relaxing nonoscillatory signals for dynamic
fluctuating moments:

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

(3)

where \(A_{AF}, A_F,\) and \(A_{\text{tail}}\) are the asymmetries associated with the three signals. Here, the subscript “AF” means an oscillatory signal due to the formation of long-range antiferromagnetic order and the subscript “F” means a fast fluctuating signal in an early time domain \((t \leq 50 \text{ ns})\) due to fast fluctuating moments. \(f_{AF}(=\omega_{AF}/2\pi)\) is the muon Larmor frequency corresponding to the static internal AF field, \(\phi_{AF}\) is the initial phase of the oscillatory signal, \(\lambda_{AF}, \lambda_F,\) and \(\lambda_{\text{tail}}\) are the exponential relaxation rates of the three signals. Furthermore, \(A_0 = 0.2408 (=A_{AF} + A_F + A_{\text{tail}})\), which is equivalent to the full asymmetry, is fixed in the whole \(T\) range below 40 K, based on a weak transverse field measurement at 40 K.

Figure 3 shows the \(T\) dependencies of the \(\mu^+\)SR parameters together with \(\chi\) measured with \(H = 100\ \text{Oe}\). As \(T\) decreases from \(T_N\), \(f_{AF}\) abruptly appears at 23 K and almost levels off to a constant value for \(T \leq 22\ \text{K}\). \(f_{AF}\) corresponds to the order parameter of the magnetic transition. Since the \(f_{AF}(T)\) curve is very similar to the \(\chi(T)\) curve, the AF transition is found to exhibit a first-order nature also from a \(\mu^+\)SR viewpoint. This suggests that the AF transition is strongly coupled with the structural phase transition at \(T_N\), because a magnetic transition is usually classified as a second-order transition.\(^\text{17}\) Except just below \(T_N\), \(\lambda_{AF}\) slightly increases with decreasing \(T\), while the magnitude of \(\phi_{AF}\) decreases towards 0. The latter usually indicates that the AF order is commensurate to the lattice.\(^\text{16}\) Even when we fixed \(\phi_{AF} = 0\) in the whole \(T\) range, the \(T\) dependence of \(f_{AF}\) was very similar to that shown in Fig. 3(b). The spin structure of the AF phase is discussed later.

Concerning the other parameters, \(A_{AF}\) increases gradually and reaches around 50\% of \(A_0\) at 1.8 K. On the other hand, \(A_{\text{tail}}\) is \(\sim 30\%\) of \(A_0\) and roughly \(T\) independent below \(T_N\), which is reasonable for the “1/3 powder tail” signal caused by the field component parallel to the initial muon-spin polarization. This is also supported by the \(\lambda_{\text{tail}}\) data, in which \(\lambda_{\text{tail}}\) is very small compared to \(\lambda_{AF}\) and \(\lambda_{AF}\) and is approaching zero when \(T \to 0\). The \(A_F\) signal, hidden in the very early time domain
remains about 25% even at 1.8 K. This suggests that the 1/3 signal in the AF phase. Since implanted muons see a rapidly fluctuating internal field even for Ag₂CrO₂ with temperature above 30 K, indicating the sample separates into two phases even above Tₙ. One (A₁) shows a fast relaxing behavior due to fluctuating magnetic moments and the other (A₂) exhibits a slow relaxing behavior as typical paramagnets. Since the “1/3 powder tail” signal also appears in the phase showing a fast relaxing behavior, the A₁ signal is divided into two signals under the condition that λ_fast > λ_slow.

At first, we fitted the ZF spectrum at each T using Eq. (4) and found that λ₂ is almost T-independent below 28 K. Then, we fitted all the ZF-spectra in the T range between 24 and 30 K using a common λ₂ parameter. Such a global fit provided that λ₂ = (0.0541 ± 0.0014) μs⁻¹. Figures 4(b) and 4(c) show the temperature dependencies of λ_fast, λ_slow, A₁/A₀, and A₂/A₀. Both λ_fast and λ_slow start to increase below T ~ 27 K, accompanied by the increase in A₁/A₀ and decrease in A₂/A₀, and becomes quite rapid as T approaches Tₙ. This result suggests that the phase with disordered moments appears below ~27 K and the volume of such phase increases with decreasing T together with the evolution of the disordered moments. Finally, the whole volume becomes the phase with disordered moments and static long-range order completes below Tₙ. Also, below Tₙ, the A₂ signal falls into the Aₚ signal [see Fig. 3(e)], as in the case for NaNiO₂. This scenario is consistent with that proposed by inelastic neutron scattering measurements.¹⁰

V. DISCUSSION

A. Ag₂CrO₂

In order to conjecture the AF spin structure for Ag₂CrO₂, the muon site(s) in the lattice were at first calculated. Such information was extracted from the distribution of electrostatic potential obtained by first-principles calculations²¹ based on density-functional theory (DFT) with generalized gradient approximation (GGA). As a result, the implanted muons are expected to locate above the center of the triangular lattice of the O ions. The three distances between μ⁺ and O, which locates at the center of the triangle, are 1.6931, 1.6931, and 1.9145 Å. In other words, the atomic position of the implanted muon is (0.1978, 0.5000, 0.1782) in a monoclinic setting (see Fig. 5). The distance to the nearest neighboring O ions is rather long compared with a typical distance (~1 Å) in many oxides, probably due to a metallic nature of Ag₂CrO₂. Note that the predicted electrostatic potential for the above muon site is lower by ~2 eV than that for the interstitial site in the Ag₂ plane. Thus all the implanted muons are expected to locate near the O ions in the lattice.

Neutron diffraction (ND) measurements¹⁰ revealed the appearance of magnetic Bragg peaks indexed by $\frac{1}{3} L$ and $\frac{1}{3} L$, where L = 0 or 1, in a monoclinic setting. For the AF spin structure with the 5 × 5 lattice, a partially disordered AF (PDA) state was proposed,¹⁰ as shown in Fig. 6(a). The other state, in which the AF wave vector is modulated both along the a and b axes with the propagation vector k = (⁴⁄₃, ⁴⁄₃, 1) (MAF), is also available for explaining the appearance of

\[ A₀ P_{ZF}(t) = A₁ \left[ \frac{1}{3} \exp(-\lambda_{fast} t) + \frac{1}{3} \exp(-\lambda_{slow} t) \right] + A₂ \exp(-λ₂t) \] (4)
For the PDA state, there are ten disordered Cr spins in the 5 × 5 lattice. Here, we assume that the ten Cr spins are randomly arranged parallel (up) or antiparallel (down) to the c axis, but the net moment is zero below $T_S$. This is because the magnetic nature below $T_S$ is basically AF; that is, the saturated magnetization, estimated by an $M$–$H$ loop at 2 K, is only about 0.08$\mu_B$/Cr.9 Therefore we need to calculate $H_{int}$ for the all cases that five spins among the ten disordered sites are up (u) and the rest five spins are down (d) in Fig. 6(a); namely, uuuuuddddd, uuuddudddd, uuuddudddd,.... This corresponds to the combination for selecting five from ten. Thus a total number of the combination for the spin arrangement in the PDA state (N) is given by $N = 10C5 = \frac{10!}{5!(10-5)!}$. Using the muon sites deduced by DFT calculations under the whole combination for the PDA spin arrangements, we obtain the distribution of $H_{int}$ for PDA by dipole field calculations using the DipElec program.22 We call this PDA state a “static-PDA” state. On the contrary, we could consider a “dynamic-PDA” state, in which the disordered Cr spins are too rapidly fluctuating to be seen by $\mu^+SR$. This means that the magnitude of the ten disordered Cr spins is eventually 0.

Figure 7 shows the calculated distribution of $H_{int}$ for the two PDA and MAF states together with the Fourier transform of the ZF-$\mu^+SR$ time spectrum at 1.8 K. This clearly demonstrates that the PDA state is more reasonable than the MAF state for explaining the present $\mu^+SR$ result. If we compare the $H_{int}/\mu_C$ at which $\frac{1}{T} \sum_{i=1}^{n} D_i = 0.5$ with $H_{int}$ at which $\int_{0}^{t} A_{real}dt = 0.5 \times 100$ MHz $A_{real}dt$, the ordered Cr moment ($\mu_C$) is evaluated as 1.5(1)$\mu_B$ [1.8(1)$\mu_B$] at 1.8 K for a static-PDA state [a dynamic-PDA state]. These values are rather small compared with that for the ordered site estimated by neutron scattering for $T = 4$ K [$\mu_C^{ND} = 2.9(1)\mu_B$].10 Such discrepancy is probably due to the difference of time-windows between $\mu^+SR$ and ND, as in the case of $\beta''$-LiFeO$_2$.23 In fact, $\mu^+SR$ detected a rapidly relaxing signal for Ag$_2$CrO$_2$ even at the lowest $T$ measured [see Figs. 2(a), 3(e), and 3(f)], which would correspond to an “invisible” part of the ordered magnetic moment within a $\mu^+SR$ time window.

More correctly, for the materials with static AF order, such as, BaCoO$_3$,24 Li$_2$MnO$_3$,25 and Ag$_2$NiO$_2$ (see Sec. V C), the ordered moment estimated by $\mu^+SR$ was found to be comparable to that by ND. Therefore the difference between $\mu_C^{SR}$ and $\mu_C^{ND}$ implies that the PDA state in Ag$_2$CrO$_2$ is dynamic, since each Cr spin is equivalent. In other words, Fig. 7(a) is a snap shot of the spin arrangement, and each spin would change polarity and order/disorder in the next moment. The fluctuation of the disordered spin is too fast to be visible even by ND,10 while those for the ordered spin is thought to range in the time-window between ND and $\mu^+SR$.

The above discussion provides us a hint which PDA state is more suitable for the ground state of Ag$_2$CrO$_2$. Although there is no direct evidence to support one of the two, the existence of the fast relaxing signal ($\Delta f$) even at the lowest $T$ measured [see Fig. 3(e)] and the fact that $\mu_C^{SR} < \mu_C^{ND}$ suggest that a dynamic-PDA state is more acceptable for Ag$_2$CrO$_2$, as expected from ND.10 This is because, for a dynamic-PDA state, we assumed the average magnitude of the ten disordered Cr spins is 0, since they are rapidly fluctuating. Therefore, making comparison with the muons close to the ordered Cr spins, the muons sitting close to the disordered Cr spins are
Returning to Ag₂CrO₂, the formation of a PDA state suggests the presence of a ferromagnetic (FM) chain along the c axis. A strong hybridization of Cr 3d with Ag 5s orbital is naturally thought to be an essential factor to induce an FM interlayer coupling through the [Ag₂] plane. However, since the AF interlayer coupling is predominant for the related compound Ag₂NiO₃ probably mediated by an RKKY interaction of conduction electron in the [Ag₂] plane, it is not simple to explain the origin of an FM coupling in Ag₂CrO₂. In addition, the electron configuration of the Cr³⁺ ion is represented by $t_{2g}^3$, meaning the lack of orbital degree of freedom. In fact, the distortion of the Cr triangular lattice is rather small compared with that for Ag₂MnO₃. Furthermore, the DFT calculations used for the prediction of muon sites reveal that the stability of the FM ordered phase is almost the same to that for the A-type AF ordered phase, if we assume an FM coupling between the neighboring Cr spins. Therefore we need further theoretical and experimental studies on the layered chromium dioxides and disilver transition-metal dioxides in order to understand the origin of the PDA state in Ag₂CrO₂. Since Yoshida and coworkers recently found a fourth derivative, Ag₂FeO₂, it is highly desirable to investigate its magnetic nature by ND and $\mu^+\text{SR}$.

C. Ag₂NiO₂

In our previous $\mu^+\text{SR}$ study on Ag₂NiO₃, we only noted the presence of two damped oscillatory signals with different frequencies. Also, based on the delay of the initial phase, incommensurate AF order was proposed for the magnetic ground state below $T_N$. Here, we attempt to estimate $H_{\text{int}}$ in Ag₂NiO₂ using the same muon site as in Ag₂CrO₂ and the AF spin structure determined by ND.³ As a result, we obtained the

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**FIG. 7.** (Color online) Dipolar field distribution for (a) a static-PDA, (b) dynamic-PDA, and (c) modulated AF (MAF) states, and (d) the Fourier transformed frequency spectrum of the ZF-$\mu^+\text{SR}$ time spectrum at 1.8 K for Ag₂CrO₂. In (a)–(d), blue solid lines represent the integral of the number density or amplitude.

expected to feel a fast relaxing $H_{\text{int}}$ and are responsible to the $A_F$ signal hidden in the very early time domain ($t \leq 50$ ns).

**FIG. 8.** (Color online) (a) dipolar field distribution for modulated AF state and (b) the Fourier transformed frequency spectrum of the ZF-$\mu^+\text{SR}$ time spectrum at 1.9 K for Ag₂NiO₂.
following two $H_{\text{int}}$: namely, $H_{\text{int1}}/\mu_{\text{Ni}} = 2771 \text{ (Oe/}\mu_{\text{B}})$ and $H_{\text{int2}}/\mu_{\text{Ni}} = 3469 \text{ (Oe/}\mu_{\text{B}})$. The ratio of the number density between the two $H_{\text{int}}(N_1/N_2)$ is 0.5 (see Fig. 8). The ordered Ni moment is, thus, estimated as $\mu_{\text{Ni}} = (0.571 \pm 0.016)\mu_{\text{B}}$ at 1.9 K, which is comparable to the ND result at 5 K ($0.67\mu_{\text{B}}$).\(^5\)

Although the presence of the two oscillatory signals are reasonably reproduced by the above dipole field calculations, it is still difficult to explain the delay of the initial phase. However, the wide field distribution in the frequency spectrum [see Fig. 8(b)] implies that the ZF spectrum includes not only the above two signals but also other signals with different oscillation frequencies, probably due to deviation of the muon site from the prediction. For such case, the fit using a combination of two cosine signals used in Ref. 6 would provide a significant delay in an initial phase, even when each signal has no delay, as in the case for LiCrO$_2$.\(^3\)

This could be a reason for the delay in $\phi_{\text{AF}}$ for Ag$_2$NiO$_2$.

Finally, it would be useful to compare the $\mu^{+}$SR result for Ag$_2$NiO$_2$ with those for AgNiO$_2$ with $T_N = 20$ K. The AF wave vector for AgNiO$_2$ was found to be modulated along the $a$-axis with the propagation vector $k = (1/2, 0, 0)$.\(^3\) However, due to charge disproportionation of Ni$^{3+}$ ions, the proposed AF spin structure is very complicated\(^3\) leading to the observation of six distinct muon-spin precession frequencies below $T_N$ without delay of each initial phase.\(^3\) On the contrary, such charge disproportionation is not observed for Ag$_2$NiO$_2$,\(^5\) probably due to a metallic nature of the [Ag$_2$] plane and a hybridization between 3$d$ and 5$s$ orbitals.\(^4\) This arises the special interest on the magnetic ground state of Ag$_2$MO$_2$, which we have attempted to elucidate with both muons and neutrons.

VI. SUMMARY

We have investigated the magnetic nature of Ag$_2$CrO$_2$ with $\mu^{+}$SR and found the formation of static long-range antiferromagnetic (AF) order below $T_N = 24$ K. Based on dipole field calculations at the muon site, which is predicted by DFT calculations, the observed distribution of an internal magnetic field was reasonably explained by the partial disordered antiferromagnetic order with $5 \times 5$ lattice proposed by neutron scattering.

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35 F. Xiao, T. Lancaster, P. J. Baker, F. L. Pratt, S. J. Blundell, J. S. Möller, N. Z. Ali, and M. Jansen, Phys. Rev. B 88, 180401(R) (2013); despite a very recent $\mu^+\text{SR}$ work on KCrO$_2$ in ISIS, the AF spin structure was still not clarified due to a limited time resolution of a pulsed muon beam.
37 H. Yoshida (private communication).