Partially disordered spin structure in Ag_2CrO_2 studied with $\mu^+\text{SR}$ Jun Sugiyama,^{1,*} Hiroshi Nozaki,¹ Kazutoshi Miwa,¹ Hiroyuki Yoshida,² Masaaki Isobe,² Krunoslav Prša,³ Alex Amato,⁴ Daniel Andreica,⁵ and Martin Månsson^{3,6}¹*Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan*²*National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*³*Laboratory for Quantum Magnetism, École Polytechnique Fédérale de Lausanne, Station 3, CH-1015 Lausanne, Switzerland*⁴*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*⁵*Faculty of Physics, Babes-Bolyai University, 3400 Cluj-Napoca, Romania*⁶*Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*

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The magnetism of a metallic two-dimensional triangular antiferromagnetic (AF) compound, Ag_2CrO_2 , has been investigated by muon-spin rotation and relaxation ($\mu^+\text{SR}$) using a powder sample in the temperature range between 1.8 and 40 K. Below $T_N = 24$ K, a muon-spin precession signal was clearly observed in the zero-field spectrum, indicating the formation of static AF order. It was also found that the internal field is temperature independent except for in the vicinity of T_N , as in the case for the susceptibility versus temperature curve. This suggests that the AF transition is induced by a first-order structural phase transition at T_N . Combining the $\mu^+\text{SR}$ result with the prediction for muon sites in the lattice by first-principles calculations, a partially disordered AF state was found to be the most reasonable spin structure for Ag_2CrO_2 .

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I. INTRODUCTION

Disilver transition-metal dioxides, Ag_2MO_2 with $M = \text{Ni}$ and Mn , which consist of alternating stacks of $[\text{Ag}_2]^{+1}$ and $[\text{MO}_2]^{-1}$ 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 $[\text{Ag}_2]$ plane is thought to be responsible for the metallic conductivity, recent soft x-ray photoemission and absorption spectroscopy measurements on Ag_2NiO_2 and Ag_2MnO_2 revealed a contribution from the $3d$ electrons of Ni and Mn on the density of states at the Fermi level (E_F).⁴ 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 MO_2 planes through the superexchange interaction via an $M\text{-O-(Ag}_2\text{)-O-M}$ pathway.

Indeed, a very recent neutron diffraction (ND) experiment on Ag_2NiO_2 ⁵ clarified that the magnetic structure is a modulated A-type AF, in which Ni spins align antiparallel along the c -axis through the $[\text{Ag}_2]$ plane. Muon-spin rotation and relaxation ($\mu^+\text{SR}$) experiments also suggested the presence of long-range AF order below $T_N = 22$ K, but such order is likely to be incommensurate with the lattice.⁶ On the contrary, for Ag_2MnO_2 , ND experiment proposed the formation of a short-range collinear state below $T \sim 40$ K due to a very weak magnetic correlation along the c axis,⁷ eventually quasi one-dimensional along the b -axis. The absence of long-range order was confirmed also by $\mu^+\text{SR}$, but short-range order was found to appear below 31 K.⁸ Therefore the magnetic nature of Ag_2MO_2 is strongly dependent on M , despite the presence of the $[\text{Ag}_2]$ plane between the adjacent $[\text{MO}_2]$ planes.

Recently, a third Ag_2MO_2 compound, i.e., Ag_2CrO_2 has been prepared for the first time using a high-pressure synthesis technique and found to exhibit an AF transition at 24 K,⁹ along with a simultaneous structural phase transition from a high- T trigonal phase to a low- T monoclinic phase.¹⁰ A

sudden decrease of the electrical resistivity at T_N suggests a strong hybridization of Cr $3d$ with Ag $5s$ orbital,⁹ as found for Ag_2NiO_2 .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 ND¹⁰ and the proposed magnetic structure was a partial disordered AF (PDA) state with 5×5 unit cells in the ab plane.

The PDA state was already reported to appear in the Ising chain systems, such as $\text{Ca}_3\text{Co}_2\text{O}_6$ ¹¹ and $\text{Ca}_3\text{CoRhO}_6$.¹² The $\mu^+\text{SR}$ spectrum for these compounds under zero magnetic field (ZF) exhibits a very rapidly damped oscillation^{13–15} due to a wide distribution of the internal magnetic field (H_{int}) at the muon site(s). $\mu^+\text{SR}$ is particularly sensitive to the local magnetic environment, since the μ^+ mainly feels the H_{int} created by its nearest neighbors. Therefore $\mu^+\text{SR}$ is a very good tool to confirm whether a PDA state is realized in Ag_2CrO_2 below T_N .

Here, we report the results of ZF- $\mu^+\text{SR}$ experiments on a polycrystalline Ag_2CrO_2 sample at temperatures between 1.8 and 40 K. By combining the $\mu^+\text{SR}$ 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 $\mu^+\text{SR}$ ⁶ results for the AF structure in Ag_2NiO_2 using the information on the muon site for Ag_2CrO_2 .

II. EXPERIMENTAL

A powder Ag_2CrO_2 sample was prepared at the National Institute for Materials Science (NIMS) by a solid-state reaction technique using reagent grade Ag, Ag_2O , and Cr_2O_3 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,

FIG. 1. (Color online) Temperature dependence of (a) magnetic susceptibility ($\chi = M/H$) and (b) $1/\chi$ for Ag_2CrO_2 . The χ data were obtained in field cooling (FC) mode with $H = 10$ kOe. In (b), the red solid line represents a linear fit in the T range between 200 and 400 K using the Curie-Weiss formula.

the sample was single phase of trigonal symmetry with space group $P\bar{3}m1$. The structural and physical properties of Ag_2CrO_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 ($\Theta_{\text{CW}} = -80 \pm 4$ K), and effective magnetic moment ($\mu_{\text{eff}} = 3.39 \pm 0.03 \mu_B$) were extracted from the $\chi(T)$ curve by fitting to a Curie-Weiss law, $\chi = \chi_0 + C/(T - \Theta_{\text{CW}})$ and $C = (N\mu_B^2/3k_B)\mu_{\text{eff}}^2$ in the T range between 200 and 400 K. Here, N is the number density of Cr spins, g is the Landé g factor, μ_B is the Bohr magneton, and k_B is Boltzmann's constant. The obtained values are consistent with those from literature.⁹

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 $1 \times 1 \text{ cm}^2$ 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.¹⁶

III. $\mu^+\text{SR}$ TECHNIQUE¹⁶

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, $f = (\gamma_\mu/2\pi)H_{\text{int}}$, where $\gamma_\mu/2\pi$ ($=13.554 \text{ kHz/Oe}$) is the muon gyromagnetic ratio. Such oscillation in the ZF spectrum

is represented by

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

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. $P_{\text{ZF}}(t)$ is the muon spin polarization function under ZF.

Both $G_x(t)$ and $G_z(t)$ are the relaxation function caused by inhomogeneous distribution of H_{int} at the muon sites. Here, $G_z(t)$ corresponds to the relaxation of H_{int} parallel to the initial muon-spin direction (S_μ) and shows only dynamic depolarization, while $G_x(t)$ corresponds to the relaxation of $H_{\text{int}} \perp S_\mu$ and includes both static and dynamic depolarization. The $G_z(t)$ component is usually called as a “1/3” tail signal.

For the case that the spacial modulation of H_{int} is commensurate (C) to the lattice, ϕ should be zero, because each muon stops at a certain crystallographic site in the lattice. However, for a static incommensurate (IC) magnetic order, since each muon senses a slightly different field due to mismatch of the period between muon sites and H_{int} , Eq. (1) is no longer appropriate for the oscillatory signal of the IC order, resulting in a delay of ϕ about 40° . On the contrary, such delay of ϕ is sometimes a good indicator whether the magnetic order is C or IC.

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

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

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_2CrO_2 recorded at temperatures between 1.8 and 24 K. A clear oscillatory signal is observed below 24 K ($=T_N$), 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_2NiO_2 ⁶ and Ag_2MnO_2 ⁸ obtained at the lowest T measured [see Fig. 2(b)], the AF spin structure for Ag_2CrO_2 is likely to be similar to that for Ag_2NiO_2 .

The ZF spectra for Ag_2CrO_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

FIG. 2. (Color online) (a) Examples of the ZF- μ^+ SR spectra for Ag_2CrO_2 recorded at different temperatures and (b) the ZF- μ^+ SR spectrum for Ag_2NiO_2 and Ag_2MnO_2 obtained at the lowest T measured. Solid lines in (a) represent the fit result using Eq. (3).

fluctuating moments:

$$A_0 P_{\text{ZF}}(t) = A_{\text{AF}} \cos(2\pi f_{\text{AF}} t + \phi_{\text{AF}}) \exp(-\lambda_{\text{AF}} t) + A_{\text{F}} \exp(-\lambda_{\text{F}} t) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t), \quad (3)$$

where A_{AF} , A_{F} , and A_{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 relaxing signal in an early time domain ($t \leq 50$ ns) due to fast fluctuating moments. $f_{\text{AF}} (\equiv \omega_{\text{AF}}^{\mu} / 2\pi)$ is the muon Larmor frequency corresponding to the static internal AF field, ϕ_{AF} is the initial phase of the oscillatory signal, λ_{AF} , λ_{F} , and λ_{tail} are the exponential relaxation rates of the three signals. Furthermore, $A_0 = 0.2408 (= A_{\text{AF}} + A_{\text{F}} + A_{\text{tail}})$, 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 μ^+ SR parameters together with χ measured with $H = 100$ Oe. As T decreases from T_{N} , f_{AF} abruptly appears at 23 K and almost levels off to a constant value for $T \leq 22$ K. f_{AF} corresponds to the order parameter of the magnetic transition. Since the $f_{\text{AF}}(T)$ curve is very similar to the $\chi(T)$ curve, the AF transition is found to exhibit a first-order nature also from a μ^+ SR viewpoint. This suggests that the AF transition is strongly coupled with the structural phase transition at T_{N} , because a magnetic transition

FIG. 3. (Color online) T dependencies of (a) χ (b) the muon-spin precession frequency for the A_{AF} signal (f_{AF}), (c) the exponential relaxation rate for the A_{AF} signal (λ_{AF}), (d) the initial phase of the oscillatory signal (ϕ_{AF}), (e) the normalized asymmetries (A_i/A_0), and (f) the exponential relaxation rates for the A_{F} and A_{tail} signal (λ_i) for Ag_2CrO_2 . The χ data were obtained in both field cooling (FC) and zero-field cooling (ZFC) modes with $H = 100$ Oe. At 24 K, the oscillatory signal (A_{AF}) disappears, but a third nonoscillatory relaxing signal appears instead, as explained in Sec. IV B.

is usually classified as a second-order transition.¹⁷ Except just below T_{N} , λ_{AF} slightly increases with decreasing T , while the magnitude of ϕ_{AF} decreases towards 0. The latter usually indicates that the AF order is commensurate to the lattice.¹⁶ Even when we fixed $\phi_{\text{AF}} = 0$ 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_{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 λ_{tail} data, in which λ_{tail} is very small compared to λ_{AF} and λ_{F} and is approaching zero when $T \rightarrow 0$. The A_{F} signal, hidden in the very early time domain

FIG. 4. (Color online) (a) the variation of the ZF-μ⁺SR spectrum for Ag₂CrO₂ with temperature above T_N and temperature dependencies of (b) λ_{fast} and λ_{slow} , and (c) normalized asymmetries (A_1/A_0 and A_2/A_0). In (a), solid lines represent the fitting result using Eq. (4). The data in (b) and (c) were obtained by global fitting of the ZF spectra using Eq. (4), where $\lambda_2 = (0.0541 \pm 0.0014) \mu s^{-1}$.

($t \leq 50$ ns) in Fig. 2(a), decreases with decreasing T , but still remains about 25% even at 1.8 K. This suggests that 1/4 of the implanted muons see a rapidly fluctuating internal field even in the AF phase. Since λ_F as well as f_{AF} are T -independent, it is plausible to assume that they have the same origin, i.e., the appearance of the AF ordered state.

B. Above T_N

Figure 4(a) shows the ZF-μ⁺SR spectra recorded at temperatures above T_N . Although the ZF spectrum obtained at 30 K exhibits a slow relaxation in the whole time domain, a fast relaxing component appears for $T \leq 26$ K, indicating the presence of a critical phenomenon towards T_N . For such case, the ZF spectra above T_N is usually fitted by a power exponentially relaxing signal; $A_0 P_{ZF}(t) = A_1 \exp[-(\lambda_1 t)^p]$, as in a dense-moment disordered magnetic system^{18,19} in a paramagnetic state. However, for Ag₂CrO₂, the ZF spectra were not fitted satisfactory by a single power exponentially relaxing signal but by a combination of three exponential relaxing signals:

$$A_0 P_{ZF}(t) = A_1 \left[\frac{2}{3} \exp(-\lambda_{fast} t) + \frac{1}{3} \exp(-\lambda_{slow} t) \right] + A_2 \exp(-\lambda_2 t) \quad (4)$$

where $\frac{2}{3}A_1$, $\frac{1}{3}A_1$, and A_2 are the asymmetries associated with the three signals and λ_{fast} , λ_{slow} , and λ_2 are the exponential relaxation rates of the two signals. The physics behind Eq. (4) is that the sample separates into two phases even above T_N ; one (A_1) shows a fast relaxing behavior due to fluctuating magnetic moments and the other (A_2) 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 A_1 signal is divided into two signals under the condition that $\lambda_{fast} > \lambda_{slow}$.

At first, we fitted the ZF spectrum at each T using Eq. (4) and found that λ_2 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 λ_2 parameter. Such a global fit provided that $\lambda_2 = (0.0541 \pm 0.0014) \mu s^{-1}$. Figures 4(b) and 4(c) show the temperature dependencies of λ_{fast} , λ_{slow} , A_1/A_0 , and A_2/A_0 . Both λ_{fast} and λ_{slow} start to increase below $T \sim 27$ K, accompanied by the increase in A_1/A_0 and decrease in A_2/A_0 , and becomes quite rapid as T approaches T_N . 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 T_N . Also, below T_N , the A_2 signal falls into the A_{tail} signal [see Fig. 3(e)], as in the case for NaNiO₂.²⁰ 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 corner 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 $\frac{1}{5}\frac{1}{5}L$ and $\frac{4}{5}\frac{1}{5}L$, 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 $\mathbf{k} = (\frac{1}{5}, \frac{1}{5}, 1)$ (MAF), is also available for explaining the appearance of

FIG. 5. (Color online) Muon site in Ag_2CrO_2 deduced by DFT calculations. The atomic position of the implanted muon is (0.1978, 0.5000, 0.1782) in a monoclinic setting. Note that a monoclinic distortion is very small, i.e., $\beta = 90.0723(3)^\circ$ and $a/b = 1.74144(13)$.¹⁰ The bond between μ^+ and O^{2-} does not mean a chemical bond but represent the nearest neighboring oxygens.

such magnetic Bragg peaks [see Fig. 6(b)], as in the case for Ag_2NiO_2 with $\mathbf{k} = (1, \frac{1}{3}, \frac{1}{2})$.⁵

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_N . This is because the magnetic nature below T_N is basically AF; that is, the saturated magnetization, estimated by an M - H loop at 2 K, is only about $0.08\mu_B/\text{Cr}$.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, uuuuuddddd, uuuuuddddd,.... 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 $N = {}_{10}C_5 = \frac{10!}{5!(10-5)!}$. 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 μ^+ 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- μ^+ 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 μ^+ SR result. If we compare the $H_{\text{int}}/\mu_{\text{Cr}}$ at which $\frac{1}{n} \sum_{i=1}^n D_i = 0.5$ with H_{int} at which $\int_0^f A_{\text{real}} df = 0.5 \int_0^{100 \text{ MHz}} A_{\text{real}} df$, the ordered Cr moment (μ_{Cr}) is evaluated as $1.5(1)\mu_{\text{B}}$ [$1.8(1)\mu_{\text{B}}$] 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 [$\mu_{\text{Cr}}^{\text{ND}} = 2.9(1)\mu_{\text{B}}$].¹⁰ Such discrepancy is probably due to the difference of time-windows between μ^+ SR and ND, as in the case of β'' -LiFeO₂.²³ In

FIG. 6. (Color online) Schematic spin arrangement with 5×5 lattice for (a) a partially disordered AF (PDA) state and (b) a modulated AF (MAF) state and the spatial modulation of the Cr moment. Only Cr ions are shown for simplicity. In (a) and (b), the small rectangle represents a monoclinic unit cell.

fact, μ^+ SR detected a rapidly relaxing signal for Ag_2CrO_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 μ^+ SR time window.

More correctly, for the materials with static AF order, such as, BaCoO_3 ,²⁴ Li_2MnO_3 ,²⁵ and Ag_2NiO_2 (see Sec. VC), the ordered moment estimated by $\mu^+\text{SR}$ was found to be comparable to that by ND. Therefore the difference between $\mu_{\text{Cr}}^{\text{SR}}$ and $\mu_{\text{Cr}}^{\text{ND}}$ implies that the PDA state in Ag_2CrO_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 $\mu^+\text{SR}$.

The above discussion provides us a hint which PDA state is more suitable for the ground state of Ag_2CrO_2 . Although there is no direct evidence to support one of the two, the existence of the fast relaxing signal (A_F) even at the lowest T measured [see Fig. 3(e)] and the fact that $\mu_{\text{Cr}}^{\text{SR}} < \mu_{\text{Cr}}^{\text{ND}}$ suggest that a dynamic-PDA state is more acceptable for Ag_2CrO_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

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- μ^+ SR time spectrum at 1.8 K for Ag_2CrO_2 . In (a)–(d), blue solid lines represent the integral of the number density or amplitude.

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

B. Other chromium dioxides

In order to discuss the magnetic nature of Ag_2CrO_2 , it is helpful to know the situation of related layered chromium dioxides, such as LiCrO_2 , NaCrO_2 , and KCrO_2 . According to ND measurements,²⁶ LiCrO_2 is known to enter into an almost ideal 120° structure characteristic of the nearest-neighbor Heisenberg model on a two-dimensional triangular lattice below $T_N = 61.2$ K. This was supported by other measurements^{27–29} including μ^+ SR.^{30,31} On the other hand, NaCrO_2 lacks long-range magnetic order down to the lowest T measured, but shows an onset of gradual freezing at $T_f = 41$ K.^{32,33} For KCrO_2 , which was very recently synthesized,³⁴ susceptibility and heat capacity measurements indicated the presence of an AF transition at 23 K. Therefore, besides KCrO_2 , due to absence of information on the AF spin structure,³⁵ the interlayer coupling between Cr moments through Li or Na is very weak compared with the in-plane coupling. Furthermore, first-principles calculations predict that the interlayer coupling in LiCrO_2 is AF.³⁶

Returning to Ag_2CrO_2 , 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 $[\text{Ag}_2]$ plane. However, since the AF interlayer coupling is predominant for the related compound Ag_2NiO_2 probably mediated by an RKKY interaction of conduction electron in the $[\text{Ag}_2]$ plane, it is not simple to explain the origin of an FM coupling in Ag_2CrO_2 . In addition, the electron configuration of the Cr^{3+} 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 Ag_2MnO_2 . 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 Ag_2CrO_2 . Since Yoshida and coworkers recently found a fourth derivative, Ag_2FeO_2 ,³⁷ it is highly desirable to investigate its magnetic nature by ND and μ^+ SR.

C. Ag_2NiO_2

In our previous μ^+ SR study on Ag_2NiO_2 ,⁶ 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_{int} in Ag_2NiO_2 using the same muon site as in Ag_2CrO_2 and the AF spin structure determined by ND.⁵ As a result, we obtained the

FIG. 8. (Color online) (a) dipolar field distribution for modulated AF state⁵ and (b) the Fourier transformed frequency spectrum of the ZF- μ^+ SR time spectrum at 1.9 K for Ag_2NiO_2 .⁶

following two H_{int} s; namely, $H_{\text{int1}}/\mu_{\text{Ni}} = 2771$ (Oe/ μ_{B}) and $H_{\text{int2}}/\mu_{\text{Ni}} = 3469$ (Oe/ μ_{B}). The ratio of the number density between the two H_{int} s (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 .³⁰ This could be a reason for the delay in ϕ_{AF} for Ag_2NiO_2 .

Finally, it would be useful to compare the $\mu^+\text{SR}$ result for Ag_2NiO_2 with those for AgNiO_2 with $T_{\text{N}} = 20$ K. The AF wave vector for AgNiO_2 was found to be modulated along the a -axis with the propagation vector $\mathbf{k} = (\frac{1}{2}, 0, 0)$.³⁸ However, due to charge disproportionation of Ni^{3+} ions, the proposed AF spin structure is very complicated,³⁸ leading to the observation of six distinct muon-spin precession frequencies below T_{N} without delay of each initial phase.³⁹ On the contrary, such charge disproportionation is not observed for Ag_2NiO_2 ,⁵ probably due to a metallic nature of the $[\text{Ag}_2]^+$ plane and

a hybridization between $3d$ and $5s$ orbitals.⁴ This arises the special interest on the magnetic ground state of Ag_2MO_2 , which we have attempted to elucidate with both muons and neutrons.

VI. SUMMARY

We have investigated the magnetic nature of Ag_2CrO_2 with $\mu^+\text{SR}$ and found the formation of static long-range antiferromagnetic (AF) order below $T_{\text{N}} = 24$ 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 5×5 lattice proposed by neutron scattering.

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