μ^+ SR study on ferromagnetic hollandite $\text{K}_2\text{Cr}_8\text{O}_{16}$ and $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ Jun Sugiyama,^{1,*} Hiroshi Nozaki,¹ Martin Månsson,^{2,3} Krunoslav Prša,^{2,†} Daniel Andreica,⁴ Alex Amato,⁵ Masahiko Isobe,⁶ and Yutaka Ueda⁶¹*Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan*²*Laboratory for Solid State Physics, ETH Zürich, CH-8093 Zürich, Switzerland*³*Laboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*⁴*Faculty of Physics, Babes-Bolyai University, 3400 Cluj-Napoca, Romania*⁵*Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*⁶*Materials Design and Characterization Laboratory, Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

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The magnetism of a quasi-one-dimensional ferromagnetic (FM) compound, $\text{K}_2\text{Cr}_8\text{O}_{16}$, has been investigated by muon-spin rotation and relaxation (μ^+ SR) using a powder sample in the temperature range between 2 and 225 K. Below $T_c = 163$ K, muon-spin precession signals were clearly observed in the zero-field spectrum, indicating the formation of static FM order. It was also found that the internal field does not change drastically at the metal-to-insulator transition temperature, $T_{\text{MI}} \sim 100$ K. Electrostatic potential calculations and dipole field calculations suggested that FM order is not parallel to the [100], [010], [001], and [110] directions but likely parallel to the [101], [011], and/or [111] directions. A very similar result was obtained for a related compound, $\text{Rb}_2\text{Cr}_8\text{O}_{16}$, while its T_c is 254 K.

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I. INTRODUCTION

The nature of the ground state of the quasi-one-dimensional (Q1D) spin system, having characteristic 1D zigzag chains in the structure, is attracting considerable theoretical and experimental interest.^{1–5} In these systems, there exists a competition between the nearest-neighbor (NN) and the next-nearest-neighbor (NNN) interactions. Furthermore, the interaction between the zigzag chains, i.e., the interchain interaction, plays an essential role in the formation of magnetic order/disorder in real systems, since a zigzag chain is never isolated. The spin density of the zigzag chain is another significant factor that determines the ground state of the compounds. Although theoretical treatments for zigzag chain compounds with $S = 1/2$ and $S = 1$ are available,^{6–9} there are, to the authors' knowledge, no studies on the case for $S \geq 3/2$. Furthermore, even for the case with $S \leq 1$, there exists only limited work on the ground state of the mixed valence state.¹⁰

We have therefore initiated experimental studies of the ground state of the zigzag chain compounds in order to understand how the competition among NN, NNN, and interchain interactions affects the magnetic ground state by means of positive muon-spin rotation and relaxation (μ^+ SR).^{11–13} Here, μ^+ SR is one of the most powerful techniques for detecting the magnetic order in a system, whether it is short or long ranged.

Isobe and co-workers recently reported the electronic/magnetic nature of three hollandite-type oxides ($\text{K}_2\text{M}_8\text{O}_{16}$) synthesized by a high-pressure technique; namely, $\text{K}_2\text{Ti}_8\text{O}_{16}$,¹⁴ $\text{K}_2\text{V}_8\text{O}_{16}$,¹⁵ and $\text{K}_2\text{Cr}_8\text{O}_{16}$.¹⁶ Actually, $\text{K}_2\text{V}_8\text{O}_{16}$ was originally synthesized by Okada *et al.*¹⁷ and $\text{K}_2\text{Cr}_8\text{O}_{16}$ by Endo *et al.*^{18,19} but Isobe *et al.* clarified their novel physical properties from the viewpoint of the Q1D spin system. Here, the hollandite-type oxides have a zigzag M_2O_4 chain along the c axis, and the zigzag chains are arranged so as to form irregular squares, with a K ion located in the center (see Fig. 1). It was reported that $\text{K}_2\text{Ti}_8\text{O}_{16}$ is a Pauli paramagnetic metal down to the lowest measured temperature,¹⁴ while $\text{K}_2\text{V}_8\text{O}_{16}$ has a

metal-to-insulator transition accompanied with the structural change at $T_{\text{MI}} \sim 160$ K.¹⁵ The high-temperature (T) metallic phase shows a Curie-Weiss (CW) type susceptibility (χ) with an antiferromagnetic (AF) interaction, but in the low- T insulating phase, half of the V chains were found to be dimerized so as to form spin singlets.^{15,20}

In contrast to these two hollandites, $\text{K}_2\text{Cr}_8\text{O}_{16}$ shows a CW-type $\chi(T)$ curve with a ferromagnetic (FM) interaction and exhibits an FM transition at $T_c = 180$ K.¹⁶ Below T_c , an additional metal-to-insulator transition is found at $T_{\text{MI}} = 95$ K by resistivity measurements.¹⁶ However, according to the x-ray-diffraction (XRD) analysis in an early stage, the crystal structure of $\text{K}_2\text{Cr}_8\text{O}_{16}$ was assigned to be a tetragonal symmetry with space group $I4/m$ in the T range between 10 and 300 K.¹⁶ This implies that the two transitions are purely electric or magnetic in origin. Unfortunately, $\text{K}_2\text{Cr}_8\text{O}_{16}$ can only be prepared at higher pressure (6.7 GPa) than that for $\text{K}_2\text{Ti}_8\text{O}_{16}$ and $\text{K}_2\text{V}_8\text{O}_{16}$, meaning that the sample amount is considerably limited (below 100 mg). As a result, it is very difficult to prepare large enough amounts for neutron-scattering measurements. In addition, considering the difficulty to determine an FM structure by nonpolarized neutron scattering, the muon-spin spectroscopy (μ^+ SR) is therefore expected to be a crucial tool to elucidate the magnetic nature of $\text{K}_2\text{Cr}_8\text{O}_{16}$. Here, we report the μ^+ SR result on $\text{K}_2\text{Cr}_8\text{O}_{16}$ and deduce a plausible magnetic ground state. Following upon $\text{K}_2\text{Cr}_8\text{O}_{16}$, we briefly report the μ^+ SR result on a related compound, $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ with $T_c = 295$ K.^{17,21}

II. EXPERIMENT

Polycrystalline samples of $\text{K}_2\text{Cr}_8\text{O}_{16}$ and $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ were prepared at ISSP at the University of Tokyo using a solid-state reaction technique under 6.7 GPa at 1273 K for 1 h. The detail of preparation and characterization of the sample was reported in elsewhere.^{16,17,21} The approximately 100-mg powder sample was pressed into a disk with 10 mm diameter

FIG. 1. (Color online) Crystal structure of $\text{K}_2\text{Cr}_8\text{O}_{16}$.

and 0.5 mm thickness. This disk was attached to a fork-type low-background sample holder by a very thin Al-coated Mylar tape in a liquid-He flow-type cryostat in the T range between 1.8 and 275 K. The μ^+ SR experiments were performed on the $\pi\text{M3.2-GPS}$ and $\pi\text{E1-Dolly}$ surface muon beamlines at PSI, using an experimental setup and techniques described elsewhere.²²

III. RESULTS

A. Ferromagnetic state of $\text{K}_2\text{Cr}_8\text{O}_{16}$

Figure 2 shows the zero field (ZF) μ^+ SR time spectrum at 2 K and the T variation of the Fourier transform. At 2 K, four peaks can be observed at $f_1 = 117$ MHz, $f_2 = 85$ MHz, $f_3 = 75$ MHz, and $f_4 = 35$ MHz, indicating the existence of four magnetically different muon sites in the crystal lattice. The ZF spectrum was well fitted by a combination of the four

FIG. 2. (Color online) (a) The ZF- μ^+ SR time spectrum for $\text{K}_2\text{Cr}_8\text{O}_{16}$ at 2 K and (b) the temperature dependence of Fourier power spectrum. The solid line in (a) represents the best fit using Eq. (1).

oscillatory signals and two nonoscillatory relaxing signals,

$$A_0 P_{\text{ZF}}(t) = \sum_{i=1}^4 A_{\text{FM}i} \cos(2\pi f_i t) \exp(-\lambda_{\text{FM}i} t) + A_{01} \exp(-\lambda_{01} t) + A_{02} \exp(-\lambda_{02} t), \quad (1)$$

where A_i are the asymmetries, λ_i are exponential relaxation rates, and $2\pi f_i (\equiv \omega_i)$ are the muon Larmor frequencies of the four signals. The number of oscillating components was found to depend on T , particularly below the vicinity of T_c .

At first, we fitted the ZF spectrum at each T using Eq. (1) and found that A_{01} , A_{02} , and λ_{02} are almost T independent below T_c (see Appendix V). λ_{01} is very small compared to $\lambda_{\text{FM}i}$ and decreases with decreasing T , approaching zero when $T \rightarrow 0$. Since $A_{01}/A_0 \sim 0.3$, the A_{01} signal is assigned to the “1/3 tail” signal, which is caused by the field component parallel to the initial muon-spin polarization. On the other hand, the A_{02} signal ($A_{02}/A_0 \sim 0.08$) is attributed to a small FM impurity phase, CrO_2 ,¹⁶ with $T_c^{\text{CrO}_2} \sim 390$ K.²³ On a second step, we fitted all the ZF spectra below T_c using common A_{01} , A_{02} , and λ_{02} parameters. Such a *global* fit provided that $A_{01} (= A_{\text{tail}}) = 0.0729 \pm 0.0003$, $A_{02} (= A_{\text{CrO}_2}) = 0.0186 \pm 0.0004$, and $\lambda_{02} (= \lambda_{\text{CrO}_2}) = (2.44 \pm 0.12) \times 10^6 \text{ s}^{-1}$. $A_0 \sim 0.24$ was deduced from the measurement of a reference silver sample. Thus the volume fraction of the CrO_2 phase is estimated as $\sim 8\%$ ($= 0.0186/0.24$), which is similar to the estimation from the magnetization measurements ($\sim 5\%$).¹⁶ However, $A_{\text{FM}i}$ and $\lambda_{\text{FM}i}$ still have large amount of scatter (see Appendix V). Therefore we finally attempted to fit all the ZF spectra using common $A_{\text{FM}i}$ parameters. Furthermore, since $A_{\text{FM}4}$ is very small above T_{MI} and $A_{\text{FM}3} = A_{\text{FM}2} = 0$ below the vicinity of T_c , we used four common $A_{\text{FM}i}$ below T_{MI} , three common $A_{\text{FM}i}$ between T_{MI} and 150 K, and one $A_{\text{FM}1}$ at 162.5 K.

Figure 3 shows the T dependences of the μ^+ SR parameters obtained by the global fit. The frequency versus T [$f_1(T)$] curve is found to exhibit an order-parameter-like T dependence. By using a mean-field theory below 165 K, i.e., $f_1/f_1(0\text{K}) = [(T_c^{\text{ZF}} - T)/T_c^{\text{ZF}}]^\beta$, the critical exponent (β) is estimated as 0.289(8) and T_c^{ZF} as 163.2(2)K, which is about 17 K lower than $T_c (= 180 \text{ K})$ estimated by magnetization measurements with $H \geq 500$ Oe.¹⁶ We ascribed this difference to the enhancement of the FM transition by external field. Although the T dependence of f_3 is similar to the one of f_1 , the T dependences of the other two frequencies are rather different. Furthermore, around T_{MI} , the $f_2(T)$ and $f_4(T)$ curves are merged into one, while both the $f_1(T)$ and $f_3(T)$ curves show a monotonic change with T even across T_{MI} . Although the three $f_i(T)$ curves are combined into one below the vicinity of T_c , all frequencies are found to disappear at T_c^{ZF} . This indicates the presence of multiple muon sites in the $\text{K}_2\text{Cr}_8\text{O}_{16}$ lattice, as discussed in Sec. IV.

The T dependences of $\lambda_{\text{FM}i}$ and $A_{\text{FM}i}$ suggest the slight change in the field distributions at the muons sites and possibly of their respective occupancies at T_{MI} . This indicates that the electrostatic potential of the sites in the phase below T_{MI} are rather similar to those in the phase above T_{MI} . Moreover, the total asymmetry of the oscillation signals, i.e., $\sum A_{\text{FM}i}$ is, as expected, found to be essentially constant [$\sim 0.15 = 2/3 \times (A_0 - A_{02}) = 2 \times A_{01}$] within the estimation accuracy below T_c^{ZF} . The longitudinal relaxation rate for the A_{01} signal, λ_{01} ,

FIG. 3. (Color online) T dependences of the μ^+ SR parameters for $\text{K}_2\text{Cr}_8\text{O}_{16}$; (a) muon-spin precession frequencies (f_i), (b) their relaxation rates ($\lambda_{\text{FM}i}$), (c) their asymmetries ($A_{\text{FM}i}$) and a sum of $A_{\text{FM}i}$, and (d) the relaxation rate $\lambda_{01} = \lambda_{\text{tail}}$. The data were obtained by global fitting all the ZF spectra using Eq. (1). Also, such fit provided that $A_{01} = A_{\text{tail}} = 0.0729$, and $A_{02} = A_{\text{CrO}_2} = 0.0186$. In (a), the red solid line on the $f_1(T)$ curve corresponds to $f(T) = f(0 \text{ K}) \times (1 - T/T_c)^\beta$ with $f(0 \text{ K}) = 113.0 \pm 0.8 \text{ MHz}$, $T_c = 163.2 \pm 0.2 \text{ K}$, and $\beta = 0.289 \pm 0.008$.

i.e., representing $1/T_1$ processes, is very small compared with $\lambda_{\text{FM}i}$ and is found to approach 0, when $T \rightarrow 0$, as expected for the 1/3 tail signal.

We note that complex T dependences of the spontaneous frequencies are also reported for $\text{Na}_{0.5}\text{CoO}_2$ (Refs. 24 and 25) and $\text{K}_{0.5}\text{CoO}_2$,^{26,27} for which MI transitions occur induced by charge ordering below their Néel temperature. The change in the Co valence (δ for $\text{Co}^{3.5 \pm \delta}$) induced by charge ordering was estimated to be $\delta \leq 0.2$ by NMR measurements for $\text{Na}_{0.5}\text{CoO}_2$.²⁸ This is consistent with the fact that resistivity (ρ) of $\text{Na}_{0.5}\text{CoO}_2$ ranges between 20 m Ω cm and 100 m Ω cm even at 4.2 K. Such a change in the Co valence may slightly alter the muon stopping sites through a change in the electrostatic potential in the lattice, which can result in complex $f_i(T)$ dependences.

For $\text{K}_2\text{Cr}_8\text{O}_{16}$, however, the fact that ρ reaches 400 Ω cm at 30 K (Ref. 16) would suggest a different mechanism for the MI transition than that of $\text{Na}_{0.5}\text{CoO}_2$. Indeed, a recent

first-principles calculations study on $\text{K}_2\text{Cr}_8\text{O}_{16}$ proposed that the FM nature is induced by charge ordering.²⁹ On the other hand, a very recent structural analysis on a single-crystal sample³⁰ revealed that $\text{K}_2\text{Cr}_8\text{O}_{16}$ changes its structure from a high- T tetragonal phase to a low- T monoclinic phase below ambient T , although the monoclinic distortion is very small.³¹ Furthermore, there is no indication for the formation of charge ordering in the monoclinic phase, but the MI transition is likely to be induced by a Peierls instability in the quasi-one-dimensional column structure made of four coupled Cr_2O_4 chains.³¹

The present μ^+ SR result indicates the lack of a drastic change in the microscopic magnetic environments at T_{MI} , which suggests the absence of charge ordering at T_{MI} , and, as a result, could support the scenario proposed by Toriyama *et al.*³¹

B. Paramagnetic state of $\text{K}_2\text{Cr}_8\text{O}_{16}$

In order to study the magnetic behavior above T_c , we also measured the μ^+ SR spectrum until 225 K in a weak transverse field (wTF around 50 Oe) in a field-cooling mode. Here, “weak” means that the applied field is significantly lower than any possible spontaneous internal fields (H_{int}) in the ordered state. The wTF- μ^+ SR technique is sensitive to local magnetic order via the decrease in the amplitude (asymmetry) of the μ^+ spin precession signal and the enhanced μ^+ spin relaxation.

The wTF- μ^+ SR spectrum was fitted using a combination of a slowly relaxing precessing signal and three exponentially relaxing nonoscillatory signals. The first component is due to the externally applied magnetic field (wTF = 50 Oe) and the second and third are due to H_{int} of the $\text{K}_2\text{Cr}_8\text{O}_{16}$ phase. In other words, at T below T_c , the second signal corresponds to the FM signal and the third signal to the “1/3 tail” signal. The fourth signal comes from the FM field of the CrO_2 phase:

$$A_0 P_{\text{TF}}(t) = A_{\text{TF}} \cos(2\pi f_{\text{TF}}^\mu t + \phi_{\text{TF}}) \exp(-\lambda_{\text{TF}} t) + A_{\text{FM}} \exp(-\lambda_{\text{FM}} t) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t) + A_{\text{CrO}_2} \exp(-\lambda_{\text{CrO}_2} t), \quad (2)$$

where A_0 (~ 0.24) is the initial ($t = 0$) asymmetry, $P_{\text{TF}}(t)$ is the muon-spin polarization function, f_{TF}^μ is the muon Larmor frequency corresponding to the applied wTF, ϕ_{TF} is the initial phase of the precessing signal, λ_{TF} , λ_{FM} , λ_{tail} , and λ_{CrO_2} are the exponential relaxation rates, and A_{TF} , A_{FM} , A_{tail} , and A_{CrO_2} are the asymmetries of the four components of the μ^+ SR spectrum.

Assuming that both A_{CrO_2} and λ_{CrO_2} are T independent and similar to those estimated by the ZF measurements, we obtain the T dependences of the wTF- μ^+ SR parameters, as shown in Fig. 4. The component characterized by the muon Larmor frequency is related to muons stopping in a paramagnetic phase of the sample. Its volume fraction corresponds to the ratio $A_{\text{TF}}/(A_0 - A_{\text{CrO}_2})$. Hence a clear bulk FM transition for $\text{K}_2\text{Cr}_8\text{O}_{16}$ is observed at $T_c^{\text{TF}} = 168 \text{ K}$, where the paramagnetic volume fraction reaches 0.5. Interestingly, as T decreases from 190 K, A_{TF} monotonically decreases down to $\sim 170 \text{ K}$ and then rapidly drops towards 0 at T_c^{TF} . In contrast to A_{TF} , A_{tail} appears below 190 K, increases with decreasing T , and approaches to 1/3 of $(A_0 - A_{\text{CrO}_2})$ below the vicinity

FIG. 4. (Color online) T dependences of (a) asymmetries, A_{TF} , A_{tail} , and A_{FM} , (b) relaxation rates λ_{TF} and λ_{tail} , and (c) relaxation rates λ_{TF} , λ_{tail} , and λ_{FM} . The data were obtained by fitting the wTF spectrum using Eq. (2) under the assumption that $A_{\text{CrO}_2} = 0.0186$ and $\lambda_{\text{CrO}_2} = 2.44 \times 10^6 \text{ s}^{-1}$. $T_c^{\text{TF}} (= 168 \text{ K})$ represents the temperature at which $A_{\text{TF}}/(A_0 - A_{\text{CrO}_2}) = 0.5$.

of T_c^{TF} . The A_{FM} signal is detected just below the vicinity of T_c^{TF} and rapidly increases with decreasing T .

As T decreases from 225 K, the $\lambda_{\text{TF}}(T)$ curve exhibits a critical behavior towards T_c^{TF} [Fig. 4(b)], while λ_{tail} suddenly appears around 190 K and then decreases monotonically with decreasing T . Note that it is difficult to determine the detailed T dependence of λ_{tail} , particularly at around 190 K, due to the coexistence of the A_{CrO_2} signal with $\lambda_{\text{CrO}_2} = 2.44 \times 10^6 \text{ s}^{-1}$. On the other hand, λ_{FM} is larger by two orders of magnitude than λ_{TF} and increases with decreasing T below the vicinity of T_c^{TF} , as expected from the $A_{\text{FM}i}$ signals in the ZF- μ^+ SR measurements [see Fig. 3(b)].

Overall, the wTF- μ^+ SR result indicates that disordered moments appear below ~ 190 K and develops with decreasing T , and finally long-range FM order completes below T_c^{TF} .

C. $\text{Rb}_2\text{Cr}_8\text{O}_{16}$

A related compound $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ was also reported to exhibit a ferromagnetic transition at 295 K.^{17,21} In order to compare the microscopic magnetic nature of $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ with that of $\text{K}_2\text{Cr}_8\text{O}_{16}$, we have measured the ZF- μ^+ SR spectrum for a $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ powder sample. As seen in Fig. 5(a), the ZF spectrum at 2 K for $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ seems to be identical to that for $\text{K}_2\text{Cr}_8\text{O}_{16}$ [Fig. 2(a)]. In fact, the T dependences of the major μ^+ SR parameters are found to be very similar to those for $\text{K}_2\text{Cr}_8\text{O}_{16}$, despite the fact that $T_c^{\text{ZF}} = 254.2 \pm$

FIG. 5. (Color online) (a) the ZF- μ^+ SR spectrum for $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ at 2 K and T dependences of (b) muon-spin precession frequencies (f_i) and (c) their asymmetries ($A_{\text{FM}i}$) and a sum of $A_{\text{FM}i}$. The asymmetries of nonoscillatory signals were estimated as $A_{01} = A_{\text{tail}} = 0.0727$, and $A_{02} = A_{\text{CrO}_2} = 0.0227$. The ZF spectrum was measured on the Dolly surface muon beamline in PSI. The data were obtained by global fitting all the ZF spectra using Eq. (1). In (b), the red solid line on the $f_1(T)$ curve corresponds to $f(T) = f(0 \text{ K}) \times (1 - T/T_c)^\beta$ with $f(0 \text{ K}) = 107.8 \pm 1.3 \text{ MHz}$, $T_c = 254.2 \pm 1.4 \text{ K}$, and $\beta = 0.244 \pm 0.015$.

1.4 K for $\text{Rb}_2\text{Cr}_8\text{O}_{16}$. On the other hand, the magnetization measurements with $H = 50$ Oe on the same sample used for the μ^+ SR measurements indicated that $T_c = 295$ K. It is therefore found that T_c is more strongly enhanced by external field for $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ than for $\text{K}_2\text{Cr}_8\text{O}_{16}$.

According to resistivity measurements, however, no clear indication about a metal-insulator transition temperature T_{MI} for $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ (Ref. 21) could be obtained. Although μ^+ SR is not the best method to detect such transition, the $f_3(T)$ and $f_4(T)$ curves for $\text{Rb}_2\text{Cr}_8\text{O}_{16}$ suggest a small change in magnetic environments in the T range between 125 and 150 K.

IV. DISCUSSION

Here, we focus on the FM nature of $\text{K}_2\text{Cr}_8\text{O}_{16}$, since its structural and physical properties have been investigated in more detail than those of $\text{Rb}_2\text{Cr}_8\text{O}_{16}$. While there are no prediction on the FM spin structure from the first-principles calculations,^{29,32} one can attempt to characterize the FM spin structure from the present μ^+ SR result. For unmagnetized ferromagnetic materials in zero applied field, the internal

FIG. 6. (Color online) Possible muon sites for $\text{K}_2\text{Cr}_8\text{O}_{16}$ predicted by electrostatic potential calculations: (a) in the tetragonal phase, there are two sites, μ_1 and μ_2 , but (b) in the monoclinic phase, each site splits into four unequivalent sites, resulting in eight sites, i.e., μ_{11} – μ_{14} and μ_{21} – μ_{24} . The lattice parameters for the tetragonal phase at ambient temperature are reported as follows (Ref. 16): space group is $I4/m$, $a = 9.7792(7)\text{\AA}$, and $c = 2.9379(3)\text{\AA}$; those for the monoclinic phase at 20 K are as follows (Ref. 31): space group is $P112_1/a$, $a_m = 13.803(3)\text{\AA}$, $b_m = 13.803(3)\text{\AA}$, $c_m = 2.9414(8)\text{\AA}$, and $\gamma = 90^\circ$.

magnetic field at a muon site (H_μ) is represented by^{33,34}

$$\mathbf{H}_\mu = \mathbf{H}_{\text{dip}} + \mathbf{H}_L + \mathbf{H}_{\text{hf}}. \quad (3)$$

This field can be connected to the muon-spin precession frequencies through the muon gyromagnetic ratio [$f = H\gamma_\mu/(2\pi) = 0.013553(\text{MHz/Oe}) \times H(\text{Oe})$] leading to

$$f_\mu = f_{\text{dip}} + f_L + f_{\text{hf}}, \quad (4)$$

where $\mathbf{H}_{\text{dip}}$ is the dipolar field, $\mathbf{H}_L$ is the Lorentz field, $\mathbf{H}_{\text{hf}}$ is the hyperfine field, and f_μ , f_L , and f_{hf} are corresponding muon-spin precession frequencies. Furthermore, $\mathbf{H}_L$ and $\mathbf{H}_{\text{hf}}$ are connected to the saturated magnetization (M_s) and the local spin density at the muon sites (ρ_{spin}) as follows:

$$\mathbf{H}_L = 4\pi/3 \times M_s, \quad \mathbf{H}_{\text{hf}} = 8\pi/3 \times \rho_{\text{spin}}(\mathbf{r}_\mu). \quad (5)$$

TABLE I. Possible muon sites (μ_n , μ_{nm}), which locate 1 $\text{\AA}$ away from O^{2-} , the distance between μ_n (μ_{nm}) and the nearest Cr ion ($d_{\mu-\text{Cr}}$), electrostatic potential (E) at μ_n (μ_{nm}), and dipole field ($|\mathbf{H}_{\text{dip}}|$) at μ_n (μ_{nm}) determined by electrostatic potential calculations and dipole field calculations. Here, μ_n (μ_{nm}) denotes the muon site in the tetragonal (monoclinic) phase. $\mathbf{H}_{\text{dip}}$ is calculated, when the Cr moments (μ_{Cr}) align along the $[100]$, $[\bar{1}00]$, $[010]$, and $[0\bar{1}0]$ direction. Note that we use a tetragonal notation even for the monoclinic phase. The calculations were performed with the DIPELEC program (Ref. 36), based on a point-charge model. In the tetragonal (monoclinic) phase, there are magnetically 4 (16) different muon sites, while there are crystallographically 2 (8) different muon sites.

muon site	$d_{\mu-\text{Cr}}$ ($\text{\AA}$)	E (eV)	$ \mathbf{H}_{\text{dip}} /\mu_{\text{Cr}}$ $\mu_{\text{Cr}}/[100], [\bar{1}00]$ (Oe/ μ_B)	$ \mathbf{H}_{\text{dip}} /\mu_{\text{Cr}}$ $\mu_{\text{Cr}}/[010], [0\bar{1}0]$ (Oe/ μ_B)
μ_1	2.5156	-12.41	553	319
μ_2	2.0282	-9.73	1922	1316
μ_{m11}	2.5058	-12.72	299	569
μ_{m12}	2.5346	-12.48	560	331
μ_{m13}	2.5233	-12.45	317	560
μ_{m14}	2.5363	-12.44	558	322
μ_{m21}	2.0872	-9.73	1902	1306
μ_{m22}	2.0721	-10.04	1251	1934
μ_{m23}	2.0895	-9.72	1890	1299
μ_{m24}	2.0827	-9.68	1320	1914

Since $M_s = 17.7\mu_B/\text{mol K}_2\text{Cr}_8\text{O}_{16}$ at 5 K,¹⁶ $\mathbf{H}_L$ is calculated as 2450 Oe corresponding to a frequency $f_L = 33.2 \text{ MHz}$.³⁵

In order to estimate $\mathbf{H}_{\text{dip}}$ (f_{dip}), we try to determine the muon sites in the lattice using a point-charge model, since $\text{K}_2\text{Cr}_8\text{O}_{16}$ becomes an insulator below T_M . We also assume the typical bond length between μ^+ and O^{2-} observed in oxides ($d_{\mu-\text{O}} = 1 \text{ \AA}$).²² For both the tetragonal and monoclinic structures, electrostatic potential calculations suggest possible multiple muon sites (see Fig. 6 and Table I).

Dipole field calculations provide $\mathbf{H}_{\text{dip}}$ at each site using the seven (or five) FM spin models (see Fig. 7). Here, we assumed that $\mu_{\text{Cr}} = 2.25\mu_B$, i.e., the Cr moments fully order along the principal axis. Moreover, we assumed that $\mathbf{H}_L$ is common for all the muon sites. As a result, we obtain $|\mathbf{H}_{\text{dip}} + \mathbf{H}_L|$ by $[(H_{\text{dip},x} + H_{L,x})^2 + (H_{\text{dip},y} + H_{L,y})^2 + (H_{\text{dip},z} + H_{L,z})^2]^{0.5}$. Since the monoclinic distortion is very small,³¹ the predicted $|\mathbf{H}_{\text{dip}} + \mathbf{H}_L|$ s for the monoclinic phase are similar to those for the tetragonal phase (see Table I and Fig. 7), but the linewidth of each $|\mathbf{H}_{\text{dip}} + \mathbf{H}_L|$ in the monoclinic phase is likely to become broader than that in the tetragonal phase. The prediction is consistent with the fact that there is no crucial change in the μ^+ SR parameters at T_M , at which the tetragonal phase is expected to transform into the monoclinic phase. As seen in Fig. 7(b), the highest $|\mathbf{H}_{\text{dip}} + \mathbf{H}_L|$ in the monoclinic phase reaches $\sim 5 \text{ kOe}$ when $\mu_{\text{Cr}}/[100]$ or $[010]$. Here, for simplicity, a tetragonal notation was used even for the monoclinic phase.

We move to discussion on an FM spin structure and $\mathbf{H}_{\text{hf}}$. Based on symmetry analysis under the assumption of ferromagnetism, the magnetic moments would be favored to align along the $[001]$ direction in the tetragonal phase. However, in the monoclinic phase, the symmetry is lowered and the moments can reside in the ab plane. In addition, we should note that μ^+ SR detects only the magnitude of $\mathbf{H}_\mu$. In the monoclinic phase, we assume that $\mathbf{H}_{\text{hf},1}$ is common for the μ_{m1m} sites, and $\mathbf{H}_{\text{hf},2}$ is common for the μ_{m2m} sites. This is because a first-principles calculations study revealed a homogeneous distribution of the spin density of

FIG. 7. (Color online) The predicted distribution of (a) $H_{\text{dip}} + H_L$ for the tetragonal phase, (b) $H_{\text{dip}} + H_L$ for the monoclinic phase, (c) $H_{\text{dip}} + H_L + H_{\text{hf}}$ for the monoclinic phase, and (d) the Fourier transform of the ZF- μ^+ SR spectrum for $\text{K}_2\text{Cr}_8\text{O}_{16}$ at 2 K. Here, H_{dip} is the dipolar field, H_L is the Lorentz field, and H_{hf} is the hyperfine field. In (a)–(c), based on the observed FM nature (Ref. 16), we assumed that the full moment ($2.25\mu_B/\text{Cr}$ in average) aligns along the principal axis at 2 K. Also, in (a)–(c), red lines correspond to the field for the μ_{11} and μ_{m1m} sites, while black lines correspond to the μ_{12} and μ_{m2m} sites.

the Cr ion in the lattice.³¹ Furthermore, the distance between μ^+ and the nearest neighboring Cr ion ($d_{\mu-\text{Cr}}$) is roughly identical for the μ_{m1m} sites ($d_{\mu-\text{Cr}} \sim 2.52 \text{ \AA}$) and for the μ_{m2m} sites ($d_{\mu-\text{Cr}} \sim 2.08 \text{ \AA}$) (see Table I). This suggests that $|\mathbf{H}_{\text{hf},1}| < |\mathbf{H}_{\text{hf},2}|$. Finally, we assume that $\mathbf{H}_{\text{hf}}$ is negative, i.e., antiparallel to the FM ordered moment, as in the case for EuO ,³⁷ EuS ,³⁸ and other FM materials.³⁹

Therefore the internal field $|\mathbf{H}_\mu| (= |\mathbf{H}_{\text{dip}} + \mathbf{H}_L + \mathbf{H}_{\text{hf}}|)$ at each muon site is given by $[(H_{\text{dip},x} + H_{L,x} + H_{\text{hf},x})^2 + (H_{\text{dip},y} + H_{L,y} + H_{\text{hf},y})^2 + (H_{\text{dip},z} + H_{L,z} + H_{\text{hf},z})^2]^{0.5}$. For the case that $\mathbf{H}_{\text{hf},1} = -5000 \text{ Oe}$ and $\mathbf{H}_{\text{hf},2} = -9200 \text{ Oe}$, the distribution of $|\mathbf{H}_\mu|$ for each FM model is shown in Fig. 7(c). Making comparison with the experimental result [Fig. 7(d)], the FM moments are most unlikely to align along the [100], [010], [001], and [110] directions, but likely to do

FIG. 8. T dependences of the μ^+ SR parameters obtained by an individual fit; (a) A_{01} and A_{02} , (b) λ_{01} , and (c) λ_{02} for $\text{K}_2\text{Cr}_8\text{O}_{16}$.

along [101], [011], or [111] directions. The same procedure for the tetragonal phase at 137.5 K also supports the FM structure along the [111] direction (see Appendix V). Here, we assumed the same T dependence for M_s , μ_{Cr} , $H_{\text{hf},1}$, and $H_{\text{hf},2}$ to that for f_1 .

Consequently, the FM order along the [101], [011], and [010] directions is predicted as the most probable spin structure both for tetragonal and monoclinic phase. It should be noted that these calculations were performed only for the fully disordered state, in which all the Cr ions are in a mixed valence ($+3.75$) state with $M_{\text{Cr}} = 2.25\mu_B$; namely, the uniform charge and spin distribution in the whole Cr sites. On the contrary, when the regular Cr sites are randomly occupied with Cr^{3+} by 25% and with Cr^{4+} by 75%, i.e., for the random but charge separation state, there are too many muon sites with different H_μ to yield muon-spin precession signals. As a result, it is most unlikely to observe the oscillatory signals but likely to observe a highly damped nonoscillatory signal. In other words, the appearance of the muon-spin precession signals indicates that muons *feel* H_μ in a periodic structure with a μ^+ SR spatial scale.

V. SUMMARY

In summary, thanks to the unique power of μ^+ SR, we have clarified the magnetic nature of $\text{K}_2\text{Cr}_8\text{O}_{16}$. That is, we found the formation of a static magnetic order below $T_c = 164 \text{ K}$ and probably the absence of a charge-ordered state down to 2 K, based on the analysis of the ZF spectrum. Also, we proposed an FM ground state with an easy magnetization axis parallel to the [101], [011], and/or [111] direction. A very similar result was obtained for $\text{Rb}_2\text{Cr}_8\text{O}_{16}$, although its T_c is 255 K. We wish to emphasize that a 100-mg sample was enough to obtain these results.

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FIG. 9. (Color online) T dependences of the μ^+ SR parameters for $\text{K}_2\text{Cr}_8\text{O}_{16}$ using common A_{01} , A_{02} , and λ_{02} , i.e., the result of the second step; (a) f_i , (b) $\lambda_{\text{FM}i}$, (c) $A_{\text{FM}i}$, and (d) a sum of $A_{\text{FM}i}$, A_{01} , and A_{02} , where $A_{01}(=A_{\text{tail}}) = 0.0729 \pm 0.0003$ and $A_{02}(=A_{\text{CrO}_2}) = 0.0186 \pm 0.0004$. Also, $\lambda_{02} = (2.44 \pm 0.12) \times 10^6 \text{ s}^{-1}$.

involving crystal structure were made with VESTA.⁴⁰ D.A. acknowledges financial support from the Romanian UEFIS-CDI Project No. PN-II-ID-PCE-2011-3-0583 (85/2011). M.I. and Y.U. were supported by a Grant-in-Aid for Scientific Research (Grant No. 22244041) from the Japan Society for the Promotion of Science. A part of this work was also supported by Grant-in-Aid for Scientific Research on Innovative Areas “Ultra Slow Muon” (Grant No. 23108003) of the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

APPENDIX A: FITTING THE SPECTRA

In order to demonstrate the reliability of the assumption that A_{01} , A_{02} , and λ_{02} are T independent, Fig. 8 shows the

FIG. 10. (Color online) (a) The predicted distribution of $\mathbf{H}_{\text{dip}} + \mathbf{H}_{\text{L}} + \mathbf{H}_{\text{hf}}$ for the tetragonal phase, and (b) the Fourier transform of the ZF- μ^+ SR spectrum for $\text{K}_2\text{Cr}_8\text{O}_{16}$ at 137.5 K. In (a), red lines correspond to the field for the μ_1 sites, while black lines correspond to the μ_2 sites.

T dependences of the μ^+ SR parameters, when we fitted the ZF spectrum at each T using Eq. (1), but without common parameters.

When we used common A_{01} , A_{02} , and λ_{02} for fitting all the ZF spectra below T_c , we obtained the T dependences of the μ^+ SR parameters of the FM phase (see Fig. 9). Although the $f_i(T)$ curves show a systematic T dependence, both $A_{\text{FM}i}$ and $\lambda_{\text{FM}i}$ are scattering in the whole T range. Furthermore, since $A_{\text{FM}4}$ ($\lambda_{\text{FM}4}$) is very small above T_{MI} compared with the other three $A_{\text{FM}i}$ ($\lambda_{\text{FM}i}$), the $A_{\text{FM}4}$ signal is most likely to disappear above T_{MI} . Hence we fitted all the ZF spectra using common $A_{\text{FM}i}$, as described in the main text.

APPENDIX B: PREDICTION FOR THE TETRAGONAL PHASE

The distribution of $|\mathbf{H}_{\mu}| (= |\mathbf{H}_{\text{dip}} + \mathbf{H}_{\text{L}} + \mathbf{H}_{\text{hf}}|)$ for the tetragonal phase (Fig. 10) was calculated using the following values: $\mu_{\text{Cr}} = 1.32\mu_{\text{B}} [= 2.25 \times (1 - \frac{137.5}{163.2})^{0.289} \mu_{\text{B}}]$, $M_s = 10.37\mu_{\text{B}}/\text{formula} [= 17.7 \times (1 - \frac{137.5}{163.2})^{0.289} \mu_{\text{B}}/\text{formula}]$, $H_{\text{hf},1} = -2931 \text{ Oe} [= -5000 \times (1 - \frac{137.5}{163.2})^{0.289} \text{ Oe}]$, and $H_{\text{hf},2} = -5392 \text{ Oe} [= -9200 \times (1 - \frac{137.5}{163.2})^{0.289} \text{ Oe}]$. A comparison between the prediction and the experimental result suggests that, for the tetragonal phase, the FM spin structure along the [111] direction is the most probable one among the five structures.

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