**High-field multifrequency ESR in the S=5/2 kagome-lattice antiferromagnet KFe[subscript 3](OH)[subscript 6](SO[subscript 4])[subscript 2]**

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High-field multifrequency ESR in the $S = \frac{5}{2}$ kagome-lattice antiferromagnet KFe$_3$(OH)$_6$(SO$_4$)$_2$

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We have performed high-field multifrequency electron spin resonance (ESR) and high-field magnetization measurements in magnetic fields $H$ of up to 53 T on single crystals of the kagome-lattice antiferromagnet KFe$_3$(OH)$_6$(SO$_4$)$_2$. We have analyzed the magnetization curve and the ESR excitation modes for $H||c$ by using two kinds of anisotropy origins, the Dzyaloshinsky-Moriya (DM) interactions and the single-ion anisotropy, the former of which is inevitable in a kagome-lattice antiferromagnet. We obtained good agreement between experiment and calculation for the case of the DM interactions. In addition, we have clarified the origin of a field-induced metamagnetic transition observed in the magnetization curve and determined the inplane and interplane exchanges and the DM interaction parameters.

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I. INTRODUCTION

Frustrated spin systems provide a rich variety of magnetic states, such as spin-liquid,$^1$–$^3$ spin-nematic,$^4$,$^5$ and spin-ice$^6$,$^7$ states. In particular, kagome-lattice antiferromagnets have recently attracted considerable attention as highly frustrated spin systems because the corner-sharing arrangement leads to higher degeneracy of the ground state than the edge-sharing arrangement in triangular lattices. The Heisenberg antiferromagnet on the kagome lattice with the nearest-neighbor interactions is one of the most interesting subjects because we expect the realization of a kind of “spin-liquid” ground state.

In a classical limit, the ground state is expected to possess two possible spin structures, $q = 0$ and $\sqrt{3} \times \sqrt{3}$, both of which satisfy the “120° spin structure.” Furthermore, the classical ground state has a continuous degeneracy due to the “weathervane” rotation of the spins, and thus no long-range order is expected even at zero temperature.$^8$–$^{11}$ However, it has been also shown that thermal or quantum fluctuations could lift some of the continuous degeneracy known as “order by disorder.” Theoretical studies for a large spin value predicted that the ground state has the $q = \sqrt{3} \times \sqrt{3}$ spin structure, which is selected by quantum fluctuations.$^3$ On the other hand, for a small spin value, a disordered ground state such as a resonating valence bond (RVB) state is expected to be observed.

The number of reported experimental studies of Heisenberg kagome-lattice antiferromagnets is not large because model compounds are usually difficult to synthesize in single-crystal form. Recently, some experimental results of $S = 1/2$ Heisenberg kagome-lattice antiferromagnet compounds, which are [$Cu_3$(titmb)$_2$](OCOOH)$_3$)$_6$H$_2$O,$^{13}$ herbészsmithite ZnCu$_3$(OH)$_6$Cl$_2$,$^{14}$–$^{17}$ volborthite Cu$_3$V$_2$O$_7$(OH)$_2$.2H$_2$O,$^{18}$,$^{19}$ vesignieite BaCu$_3$V$_2$O$_8$(OH)$_2$,20,21 and $Al_2Cu_3SnF_{12}$ ($A = Rb, Cs$),$^{22}$–$^{24}$ were reported. They, however, are far from ideal kagome-lattice antiferromagnets because of lattice distortion, partial substitution of nonmagnetic ions, and considerably large amounts of impurities.

By contrast with these kagome-lattice antiferromagnets, jarosites, which have a chemical formula $AM_3$(OH)$_6$(SO$_4$)$_2$,$^{25}$ where $A$ is a monovalent cation and $M$ is a trivalent cation, have been considered as ideal kagome lattices. Many kinds of jarosite compounds are listed by the combination of $A^+$($Na^+, Rb^+, Ag^+, Ti^+$, NH$_4^+$, H$_3O^+$) and $M^{3+}$(Fe$^{3+}$, Cr$^{3+}$, V$^{3+}$, Al$^{3+}$, Ga$^{3+}$, In$^{3+}$) ions. KFe$_3$(OH)$_6$(SO$_4$)$_2$ with Fe$^{3+}$ ($S = 5/2$), abbreviated as K-Fe-jarosite, is one of the model compounds of a typical classical Heisenberg kagome-lattice antiferromagnet. Magnetic susceptibilities of the K-Fe-jarosite follow the Curie-Weiss law at high temperatures with negative Weiss temperature $\Theta \sim -800$ K,$^{26}$ indicating that the nearest-neighbor interaction is antiferromagnetic. Neither the lattice distortion of the kagome plane nor the partial substitution of nonmagnetic ions has been reported and, thus, this jarosite is regarded as one of the ideal frustrated spin systems. However, the K-Fe-jarosite undergoes a three-dimensional (3D) long-range order below the Neél temperature ($T_N$) 65 K.$^{26}$ The frustration parameter $f = |\Theta|/T_N$ is about 12, indicating that this compound is highly frustrated.

The magnetic structure below $T_N$ was determined to be the $q = 0$ spin structure with $+1$ spin chirality by neutron
scattering experiments,27 where spin chiralities +1 and −1 are defined as clockwise and counterclockwise spin rotations in the view of clockwise spin-site rotation, respectively. High-quality large single crystals of K-Fe-jarosite, which were made by recent development of the precipitation reaction method,28 enable us to investigate the details of kagome physics without any assumption. In a previous study,29 magnetic susceptibilities and magnetization indicated the presence of a weak ferromagnetism along the $c$ direction. Recent theoretical work30 showed that the Dzyaloshinsky-Moriya (DM) interaction would induce such canting moments, and the magnetic structure of the K-Fe-jarosite could be explained by the DM interactions. A neutron research using a single crystal of K-Fe-jarosite31 provided details of spin excitations. Spin-wave excitations were observed in the inelastic neutron scattering experiments.

As already mentioned, the K-Fe-jarosite forms an ideal kagome lattice, which remains undistorted down to sufficiently low temperatures. There are few previous reports of the experiments on a single crystal of a kagome-lattice antiferromagnet.29,31 This paper provides an in-depth study on a classical Heisenberg kagome-lattice antiferromagnet using a single crystal. ESR is mostly useful for evaluating the perturbation parameters such as the DM interaction, which inevitably results from the symmetry of the kagome lattice. Thus, it is important to evaluate the DM components from experiment because the magnitude of the DM interaction is key to understanding the nature of the K-Fe-jarosite kagome-lattice antiferromagnet. We performed magnetization and ESR measurements in magnetic fields of up to about 50 T with pulsed magnets.

In a previous paper,29 magnetic phase transition was observed near $T_N$ and was not observed at low temperatures because of the limit of magnetic field. The successive paper32 reported the results of high-field magnetization at sufficiently low temperatures. Since the combination of high-field magnetization and ESR results enables us to determine the physical parameters precisely, we have performed magnetization measurements at 4.2 K in high magnetic fields at our high magnetic field laboratory.

The paper is organized as follows. In Sec. II, crystal structures of K-Fe-jarosite and experimental methods are described. Then, experimental results of magnetization and ESR measurements are reported in Sec. III, followed by their analyses assuming two kinds of anisotropy origins in Sec. IV. We discuss how to determine the parameters and the validity. The observed magnetic structure in K-Fe-jarosite is discussed with a theory including the DM interaction in a classical kagome-lattice antiferromagnet. The final section is devoted to the conclusion.

II. EXPERIMENT

A. Crystal structure

A single-crystal sample ($\sim 2 \times 2 \times 0.5 \text{ mm}^3$) of K-Fe-jarosite used in this study was prepared by a redox-based hydrothermal method. The details of the single-crystal synthesis were reported in Refs. 28 and 29. The K-Fe-jarosite belongs to a rhombohedral system with $R\bar{3}m$ symmetry, and lattice constants are $a = b = 7.30 \text{ Å}$ and $c = 17.09 \text{ Å}$ at room temperature.33 The crystal structure consists of kagome layers of Fe$^{3+}$ ions in the $ab$ plane. These planes stack along the $c$ axis, separated by nonmagnetic layers of SO$_2$$^-$$^-$ and K$^+$, as shown in Fig. 1(a). As depicted in Fig. 1(b), the Fe$^{3+}$ ions are coordinated with two oxygen atoms from SO$_2$$^-$$^-$ and four oxygen atoms from OH$^-$$^-$ ions to form slightly distorted octahedrons. Such anisotropic structure suggests that K-Fe-jarosite has stronger interactions in the layers than those along the $c$ axis. Figures 1(c) and 1(d) indicate two types of arrangements of FeO$_6$ octahedron in this compound. The

FIG. 1. (Color online) (a) Crystal structure of K-Fe-jarosite. Hydrogen atoms are omitted for clarity. Fe$^{3+}$ ions form a kagome lattice in the $ab$ plane. (b) Arrangement of triangles in the kagome lattice along the $c$ axis and the local environment around Fe$^{3+}$ ions. The kagome Fe$^{3+}$ layers are separated by planes of nonmagnetic K$^+$ and SO$_2$$^-$$^-$ ions. (c) and (d) Arrangement of the FeO$_6$ octahedron in the nearest triangular layers along the $c$ axis. The principal axis of the octahedron is tilted from the $c$ axis, and the tilting directions of the octahedron in (c) and (d) are opposed to each other.
tilting directions of the octahedron on each triangle against the c axis change alternatively with the layers along the c axis.

B. Experimental methods

Pulsed field ESR measurements were conducted in magnetic fields ($H$) of up to 53 T at temperatures between 1.3 and 300 K by using our pulsed field ESR apparatus equipped with a nondestructive pulse magnet, a far-infrared laser (Edinburgh Instruments, FIRL100), several kinds of Gunn Oscillators, which cover the frequency range between 50 GHz and 2 THz, and an InSb detector (QMC Instruments). The ESR measurements at 1.6 K and frequencies below 500 GHz in static magnetic fields of up to 14 T were also performed by utilizing a superconducting magnet (Oxford Instruments) and a vector network analyzer (AB millimetre, MVNA). High-field magnetization measurements at 4.2 K in a magnetic field of up to 7 T was also measured with an induction method using a pick-up coil. The magnetization was measured with a nondestructive pulse magnet. The magnetization was measured with an induction method using a pick-up coil. The magnetization at 4.2 K in a magnetic field of up to 7 T was also measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL7) for the correction of magnetization measured in pulsed magnetic fields. All the experiments were carried out at KYOKUGEN in Osaka University.

III. EXPERIMENTAL RESULTS

A. High-field magnetization

Figure 2 shows a magnetization curve at 4.2 K for $H \parallel c$. The curve with a broken line drawn by the raw data indicates a bending with a convex curvature at low fields, which is probably caused by paramagnetic impurities. Thus, we subtract the paramagnetic contribution from the raw data, assuming the Brillouin function for $S = 5/2$ with the impurity content of $\sim 0.4\%$. Then, the magnetization curve by the subtracted data increases almost linearly with increasing field as shown with a solid line in Fig. 2. A steep increase, which corresponds to the magnetic transition reported previously, is observed at about 16 T. This abrupt increase of the magnetization is believed to result from a change from antiferromagnetically aligned canted moments along the c axis to ferromagnetically aligned ones. The inset of Fig. 2 shows the field derivative of magnetization curve ($dM/dH$) observed at 4.2 K for $H \parallel c$. The $dM/dH$ shows a distinct peak around $H_c = 16.4 \ T$, which we define as the critical field ($H_c$). Since there is a hysteresis near $H_c$, this magnetic transition must be a first-order phase transition.

B. High-field ESR

Figures 3(a) and 3(b) show the frequency dependence of the ESR absorption spectra for $H \parallel c$ at 1.6 K in static magnetic fields and those at 1.3 K in pulsed magnetic fields, respectively. We observed some broad resonance signals indicated by the arrows and some sharp anomalies indicated by the open circles. All the resonance fields are plotted in the frequency-field plane as shown later in Figs. 6(b) and 8(b). We detected ESR modes with zero-field gaps of about 1600 and 350 GHz. The energy branches with the zero-field gaps were observed in the previous neutron scattering experiments. We conclude that the observed ESR modes correspond to the excitation modes at the $\Gamma$ point.

IV. ANALYSES

A. Dzyaloshinsky-Moriya model

First, we analyze the frequency dependence of the ESR resonance fields and the magnetization curve, both for $H \parallel c$ orientation. In this task, we use the following spin Hamiltonian, which we call the DM model Hamiltonian because of the inclusion of the DM term as the anisotropy origin

$$
\mathcal{H} = J \sum_{(ij)} S_i \cdot S_j + J_{ij} \sum_{(lm)} S_l \cdot S_m + \sum_{(ij)} d_{ij} S_i \times S_j - g \mu_B \sum_i S_i H,
$$

where $J$ is the nearest-neighbor exchange constant in the $ab$ plane, $\sum_{(ij)}$ the summation over pairs of the nearest-neighbor spins, $S_i, S = 5/2$ spin operator of Fe$^{3+}$ at $i$ site, $J_{ij}$ the interplane exchange constant, $\sum_{(lm)}$ the summation over pairs of the nearest-neighbor spins along the c axis, $d_{ij}$ the DM vector between $i$- and $j$-site spins, $g$ the g value of Fe$^{3+}$ spin, $\mu_B$ the Bohr magneton, and $H$ the external magnetic field. When the magnetic ions form a kagome lattice, the DM interaction is imperative because of no inversion center between the neighboring sites. The direction of the DM vector is constrained and follows the rules described by Moriya. The DM vectors exist in the mirror plane between the nearest $i$ and $j$ sites in the kagome lattice as shown in Fig. 4. Here, we divide the DM vector into two components: $d_p$, the in-plane component, and $d_z$, the out-of-plane component parallel to the c axis.

Elhajal et al. and Yildirim et al. discussed the DM interaction in a jarosite. The directions of the DM vectors are different in these reports. However, the definitions of
The DM vectors are essentially identical. In this paper, we analyzed the experimental results based on Elhajal’s definition, which is different from the definitions in Ref. 32. Elhajal et al. discussed theoretically the effects of $d_c$ and $d_p$ for a classical Heisenberg kagome-lattice antiferromagnet using a mean-field approximation and a classical Monte Carlo simulation. They argued that the $d_c$ acts to create an easy-plane anisotropy. The coplanar magnetic structure is realized when this component exists, and the direction of the chirality vector is determined by the sign of $d_c$. Accordingly, $d_c > 0$ and $d_c < 0$ stabilize positive and negative chirality, respectively. In the K-Fe-jarosite, the $q = 0$ structure with positive chirality was observed in powder neutron diffraction,26 thus $d_c > 0$ acting on this system. Elhajal et al. also discussed that all the spins have a weak $c$-axis component when $d_p$ is nonzero, resulting in a weak ferromagnetism and no global rotational degeneracy. Accordingly, magnetic behavior of the K-Fe-jarosite at low temperatures seems to be described by the DM interaction. Therefore, we carried out first the analyses by taking into account the DM interaction. It is, however, impossible to explain the arrangement of the spins along the $c$ axis and magnetic transition found in the magnetization curve merely considering the intraplane exchange and the DM interactions. Hence, the weak ferromagnetic interlayer coupling $J_{\perp}$ is required for the analysis as indicated in Eq. (1). This term forces the spins to align in such a way that canted moments on two adjacent layers are directed opposite of each other, and the competition between the Zeeman energy and weak ferromagnetic interlayer coupling causes the spins on the alternating layers to rotate $180^\circ$.32 As shown in Fig. 5, the spin structure below $H_c$ can be described by a six-sublattice model, and the spin structure above $H_c$ can be described by a three-sublattice model. Then, the free energy $F$ is expressed by the following form using a mean-field approximation:

$$
F = A \sum_{(ij)} M_i \cdot M_j + B \sum_{(lm)} M_i \cdot M_m + \sum_{(ij)} dt_{ij} \cdot M_i \times M_j - \sum_{i=1} M_i \cdot H.
$$

(2)

Here, the coefficients and the vectors below $H_c$ are given by $A = 12J/[N(g \mu_B)^2]$, $B = 12J_{\perp}/[N(g \mu_B)^2]$, $dt_{ij} = 12d_{ij}/[N(g \mu_B)^2]$, and $M_i = N(g \mu_B S_i)/6$. Above $H_c$, they are written as $A = 6J/[N(g \mu_B)^2]$, $B = 6J_{\perp}/[N(g \mu_B)^2]$, $dt_{ij} = 6d_{ij}/[N(g \mu_B)^2]$, and $M_i = N(g \mu_B S_i)/3$. $N$ is the number of magnetic ions, and $M_i$ are the magnetic moments on the $i$th sublattice.
The magnetization curve is calculated from this free energy. We derive the resonance conditions by solving the equation of motion

$$\partial M_i/\partial t = \gamma [M_i \times H_i],$$

(3)

where $\gamma$ is the gyromagnetic ratio and $H_i$ a mean-field applied on the $i$th sublattice moment given by

$$H_i = -\partial F/\partial M_i.$$

(4)

To solve the equation of motion, we use a method applied for $ABX_3$-type antiferromagnets. Assuming precession motions of the sublattice moments around those equilibrium directions, we utilize the following expressions, which represent the motion of the $i$th sublattice moment:

$$M'_i = [\Delta M_{ij}, \Delta M_{i\zeta} \exp(i\omega t), \Delta M_{i\zeta} \exp(i\omega t)],$$

(5)

where $\Delta M_{ij}, \Delta M_{i\zeta} \ll |M_i|,$ and $\hat{x}, \hat{y},$ and $\hat{z}$ are the principal axes of the coordinate system on each sublattice moment. The $\hat{x}$ axis is defined to be parallel to the direction of the each sublattice moment, and the $\hat{y}$ and $\hat{z}$ axes are perpendicular to that.

As shown in Fig. 6, we obtained good agreement between experiment and calculation using the following parameters: $J/k_B = 42.3$ K, $J_1/k_B = -9.66 \times 10^{-2}$ K, $d_p/k_B = 1.62$ K, $d_c/k_B = 1.97$ K, and $g_c = 2.00$. The details of determination of these parameters will be described in the next discussion section. The $g$ value $g_c$ is determined by ESR signal at 294 K (paramagnetic phase) as will be shown later in Fig. 9. The canting angle at 0 T is evaluated at 1.23°.

B. Crystal-field (CF) model

Next, we analyze the experimental data by the following spin Hamiltonian assuming single-ion anisotropies ($D$ and $E$). We call this model a crystal-field (CF) model:

$$\mathcal{H} = J \sum_{i<j} S_i S_j + J_{1} \sum_{i<m} S_i S_m + D \sum_i (S_i^z)^2 - E \sum_i \left( (S_i^x)^2 - (S_i^y)^2 \right) - g\mu_B \sum_i S_i H,$$

(6)

where the $z'$ and $y'$ axes are taken to be parallel to O(2)-Fe-O(2) and to be in the $ab$ plane for each Fe$^{3+}$ ion, respectively. The $x'$ axis is perpendicular to the both axes as shown in Fig. 7.

The $z'$ axis is tilted from the $c$ axis about 20°. The single-ion anisotropies were discussed in a previous paper on powder neutron scattering experiment. When $D > 0$, we have an easy-plane anisotropy and $E$ determines the direction of spin in the $x'y'$ plane. Large-$D$ and small-$E$ values are expected from the crystal structure because the distortion of the FeO$_6$ octahedron along the $z'$ axis is larger than that in the $x'y'$ plane. Because of the positive $D$, the magnetic moments tend to lie in the $x'y'$ plane, which is slightly tilted from the $ab$ plane. The positive $E$ makes the magnetic moments direct to the $x'$ axis. Therefore, the magnetic system chooses the $q = 0$ structure with +1 spin chirality and ferromagnetic component.
value from the slope of the magnetization curve (the 
changes from the model 1 to 2 with an umbrella structure
and is tilted from the c axis. The y' axis is in the ab plane and the x' axis is perpendicular to the y' and z' axes.

In this manner, the single-ion anisotropies may generate spin arrangement in this study. The free energy $F$ is expressed by the following form using a mean-field approximation:

$$F = A \sum_{ij} M_i M_j + B \sum_{i \neq j} M_i M_j + K \sum_i \left(M_{C_Fi}^{\prime}\right)^2$$

$$- C \sum_i \left([M_{C_Fi}^{\prime}]^2 - \langle M_{C_Fi}^{\prime} \rangle^2\right) - \sum_i M_i H. \quad (7)$$

Here, the coefficients that are different from those in the previous section are given by $K = 6D/[N(g\mu_B)^2]$, $C = 6E/[N(g\mu_B)^2]$ below $H_c$, and by $K = 3D/[N(g\mu_B)^2]$, $C = 3E/[N(g\mu_B)^2]$ above $H_c$.

The magnetization is calculated in the same way as in the previous section. As shown in the calculation # 1 in Figs. 8(a) and 8(b), we obtain good agreement between experiment and calculation for the magnetization curve using the following parameters: $J/k_B = 42.3$ K, $J_3/k_B = -9.66 \times 10^{-2}$ K, $D/k_B = 8.29$ K, $E/k_B = 0.522$ K and the same $g_z$ value as in the analysis of the DM model. The canting angle at 0 T is evaluated at 1.21°. However, poor agreement is attained between experiment and calculation for the ESR modes, especially the high-frequency ones. We have also analyzed experimental results so that the fitting of ESR modes might be improved as much as possible in the CF model. The analytical results are shown by the calculation # 2 in Figs. 8(a) and 8(b). For this fitting, we use the following parameters: $J/k_B = 42.3$ K, $J_3/k_B = -5.51 \times 10^{-2}$ K, $D/k_B = 4.64$ K, $E/k_B = 0.322$ K, and $g_z = 2.00$. The canting angle at 0 T is evaluated at 0.70°. The agreement between the calculated and the experimental magnetization curves after the transition is not good. Accordingly, we have found that a large-$D$ value is required to explain the large magnetization jump, while a smaller-$D$ value is needed for the fit of the high ESR modes. Hence, both the high ESR modes and the magnetization curve can not be reproduced by the same parameters.

V. DISCUSSION

First, we discuss the validity of the DM model used to analyze the experimental results. In the analysis, we determine the $J$ value from the slope of the magnetization curve (the solid line in the upper panel of Fig. 2) because the slope is proportional to $1/J$. We assume that the magnetic structure changes from the model 1 to 2 with an umbrella structure upon increasing magnetic field as illustrated in the insets of Figs. 6(a) and 8(a). The magnetic transition observed at 16.4 T is interpreted as a flop of the weak ferromagnetic component.
The relational expression between the canting angle $\eta$ and the intraplane exchange and DM parameters is given by

$$\tan 2\eta = \frac{2d_p}{(\sqrt{3}J + d \perp)}.$$  \tag{8}

When $J \gg d \perp$, it is possible to approximate $\tan 2\eta = 2d_p/\sqrt{3}J$. The lowest zero-field ESR mode, which should be equivalent to the lowest zone-center spin-wave gap in the spin-wave dispersion, is described by $S\sqrt{2}|d_p|$. Therefore, we adjust the value of $d_p$ to meet both the magnitude of the magnetization step at the transition field and the zero-field value of the lowest ESR mode. Additionally, we evaluate the $d_\parallel$ from zero-field gap of the higher ESR mode. Then, we extract the value of $J_\perp$ from the comparison of the free energies between the models 1 and 2. In this analysis, we expect the $d_\parallel$ from zero-field gap of the higher ESR mode. Thus, we perform the calculations including higher-order spin Hamiltonian term $a(S_1^4 + S_2^4 + S_3^4)$. However, the calculated results are far from the experimental ones, and thus the fits are not improved. From these considerations, we conclude the CF model is not suitable for this sample.

Next, we discuss the DM components determined by these analyses. In Table I, the magnitudes of the DM components evaluated in K-Fe-jarosite and other systems are summarized. In most kagome-lattice compounds, their DM components are of the order of 1 K. The magnitude of the $d$ vector $|d|$ is roughly given by $|d| \sim (\Delta g/g)J$ (Ref. 36) where $\Delta g$ is the difference of $g$ values in the systems. As shown in Fig. 9, the $g$-value anisotropy is quite small from the observed paramagnetic resonance signals, and almost equivalent $g$ values are obtained for the $a$ axis ($g_a = 2.01 \pm 0.01$) and the $c$ axis ($g_c = 2.00 \pm 0.01$). The magnitude of the DM vector is evaluated to be $|d| \sim (\Delta g/g)J = 0.275$ K, which is about one tenth of the value obtained from our analysis. The $g$-value anisotropy of about 0.12 is required to reproduce the size of DM vector evaluated by the analysis. However, it makes little sense that such $g$-value anisotropy is present in Fe$^{3+}$ ions with the orbital momentum $L = 0$. This is the only contradiction point in the analyses by the DM model. However, we can conclude that the DM model is more suitable than the CF model for K-Fe-jarosite.

Finally, we discuss the ground state of Heisenberg kagome-lattice antiferromagnets. As described in the Introduction, theoretical studies predicted that the ground state has a $\sqrt{3} \times \sqrt{3}$ 120° spin structure for a Heisenberg kagome-lattice antiferromagnet with a large spin value, and has a “spin-liquid”-like resonating valence bond (RVB) state with a small spin value. A long-range order (LRO) was observed in most experimental studies on Heisenberg kagome-lattice antiferromagnets, such as Cr-jarosite (Cr: $S = 3/2$), hexagonal tungsten bronze(HTB)-type FeF$_3$ (Fe: $S = 5/2$), and $A_1Cu_2B_{12}F_{12}$ type materials ($Cs_2Cu_2ZrF_{12}$, $Cs_2Cu_2SnF_{12}$, and $Cs_2Cu_2HF_{12}$ (Cu: $S = 1/2$)). Neutron scattering studies on (HTB)-type FeF$_3$ clarified the $q = 0$ structure below $T_N$. In addition, previous studies on Cr-jarosite and some $A_1Cu_2B_{12}F_{12}$ indicated the presence of weak ferromagnetism. The observed $q = 0$ structure and weak ferromagnetism in K-Fe-jarosite must be ascribed to positive $d_\parallel$ and $d_\perp$, respectively. When the spin is large enough, and finite interplane interactions exist in a real compound, it exhibits a LRO. In such case, the DM interaction works as the main perturbation term to determine the ground-state spin structure below $T_N$.

On the other hand, studies carried out on herbertsmithite (Cu: $S = 1/2$), volborthite (Cu: $S = 1/2$), and zweiseitenite

| Sample                  | $|d_\parallel|$ (K) | $|d_\perp|$ (K) | $|d|$ (K) | $(\Delta g/g)J$ (K) |
|-------------------------|---------------------|----------------|----------|-------------------|
| K-Fe-jarosite           |                     |                |          |                   |
| (this study)            | 1.62                | 1.97           | 2.55     | 0.275             |
| K-Fe-jarosite (Ref. 31) |                     |                |          |                   |
|                        | 2.27                | 2.29           | 3.22     |                   |
| Ag-Fe-jarosite (Ref. 32)| 1.97                | 2.09           | 2.87     |                   |
| Herbertsmithite (Ref. 38)| 15                 | 2              | 15.1     | 30.2              |
| Cs$_2$Cu$_3$HFF (Ref. 23)|                   | 4.52           |          | 70.9              |
| Cs$_2$Cu$_3$ZrF (Ref. 23)|                   | 6.10           |          | 61.6              |
(Cu: \( S = 1/2 \), and \( \text{Rb}_2\text{Cu}_3\text{SnF}_{12} \) (Cu: \( S = 1/2 \)) reported no LRO down to sufficiently low temperatures, and thus these materials seemed to realize some kinds of “quantum spin-liquid state” or “quantum spin-solid state.” Recently, Cépas et al. theoretically investigated the effect of the DM interaction in the \( S = 1/2 \) kagome-lattice antiferromagnet and found a quantum critical point between a moment-free phase and an antiferromagnetic LRO one around \( d_c \approx 0.1J \). Accordingly, it is expected that the ground state of a Heisenberg kagome-lattice antiferromagnet is altered drastically by the DM interaction, and the value of spin.

VI. CONCLUSION

We have performed high-field magnetization and ESR measurements on a single-crystal sample of K-Fe-jarosite, which is one of the typical classical Heisenberg kagome-lattice antiferromagnets. We observed a number of ESR branches at \( 1.3 \) and \( 1.6 \) K, and a stepwise magnetization at 4.2 K for \( H \parallel c \). We conclude that the DM interaction is the most dominant perturbation term that works in this system from the analysis of the experimental results. Our experimental results (magnetization and ESR) are successfully explained by the model having the DM interaction and the interplanar interaction, and the following parameter values were obtained:

\[
\begin{align*}
J / k_B &= 42.3 \text{ K}, \ d_p / k_B = 1.62 \text{ K}, \ d_c / k_B = 1.97 \text{ K}, \ J_{\perp} / k_B = -9.66 \times 10^{-2} \text{ K}, \text{ and } g_e = 2.00. \\
\text{The magnetic transition at } 16.4 \text{ T is caused by the change of spin structure, which arises from the competition between the DM, the interplanar, and the Zeeman interaction.}
\end{align*}
\]

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APPENDIX A

As already mentioned in Sec. IV A, we analyzed experimental results by the DM model using a mean-field approximation. In this appendix, we describe the details of the analysis. In the case of model 1, Eq. (2) can be expanded using six-sublattice magnetic moments as

\[
F = -\sum_{i=1}^{6} M_i \cdot H + A(M_1M_2 + M_2M_3 + M_3M_1) + M_4M_5 + M_5M_6 + M_6M_4 + B(M_4M_5 + M_1M_6 + M_2M_3 + M_3M_4 + M_5M_6 + M_6M_4) + dt_{12}M_1 \times M_2 + dt_{23}M_2 \times M_3 + dt_{31}M_3 \times M_1 + dt_{45}M_4 \times M_5 + dt_{56}M_5 \times M_6 + dt_{64}M_6 \times M_4. \tag{A1}
\]

When the field is applied along the \( c \) axis [\( z \) axis, \( H = (0,0,H) \)], each sublattice moment turns to direct as shown in Fig. 10. Using angles shown in the figure, we express the sublattice magnetizations as

\[
M_n = M_0(\cos \theta_n \cos \eta_n, \sin \theta_n \cos \eta_n, \sin \eta_n), \tag{A2}
\]

where \( M_0 = (N/6)g\mu_B|S| \). The angles \( \theta_n \) and \( \eta_n \) are given by

\[
\begin{align*}
\theta_1 &= 3\pi/2, \quad \theta_2 = 5\pi/6, \quad \theta_3 = \pi/6, \\
\theta_4 &= \pi/2, \quad \theta_5 = 11\pi/6, \quad \theta_6 = 7\pi/6, \\
\eta_1 &= \eta_2 = \eta_3, \quad \eta_4 = \eta_5 = \eta_6.
\end{align*}
\]

The DM components are given by

\[
\begin{align*}
&dt_{12} = dt_{45} = (-\sqrt{3}dt_p/2, -dt_p/2,d_t), \\
&dt_{23} = dt_{56} = (0,dt_p,dt_z), \\
&dt_{31} = dt_{64} = (\sqrt{3}dt_p/2, -dt_p/2,dt_z).
\end{align*}
\]

By substituting Eqs. (A2), (A3), and (A4) into Eq. (A1), we have

\[
F = -H(3M_0 \sin \eta_1 + 3M_0 \sin \eta_4) \\
+ \frac{3}{4}\frac{1}{2} AM_0^2(2 - 3\cos 2\eta_1 - 3\cos 2\eta_4) \\
+ BM_0^2(3 \cos \eta_1 \cos \eta_4 + 6 \sin \eta_1 \sin \eta_4) \\
- \frac{3}{4}\sqrt{3} dt_p M_0^2(\cos^2 \eta_1 + \cos^2 \eta_4) \\
+ \frac{3}{2}\sqrt{3} dt_p M_0^2(\sin 2\eta_1 - \sin 2\eta_4). \tag{A5}
\]

The angles \( \eta_1 \) and \( \eta_4 \) are determined by \( \partial F/\partial \eta_1 = 0 \) and \( \partial F/\partial \eta_4 = 0 \) numerically. The magnetization \( M \) induced along the \( c \) axis is expressed as

\[
M = 3M_0(\sin \eta_1 + \sin \eta_4). \tag{A6}
\]

The transformation of new coordinates \( \hat{x}, \hat{y}, \) and \( \hat{z} \) system of the \( i \)th sublattice can be performed by the matrix \( \mathbf{R}_i \):

\[
\mathbf{R}_i = \begin{pmatrix}
cos \theta_i & \cos \eta_i & \sin \theta_i & \cos \eta_i & \sin \eta_i \\
-\sin \theta_i & \cos \theta_i & \sin \eta_i & 0 \\
-\cos \theta_i & \sin \theta_i & -\sin \eta_i & \cos \eta_i & \cos \eta_i
\end{pmatrix}. \tag{A7}
\]

The transformed interaction matrix is such that

\[
M_i' = R_i M_i, \quad M_i = R_i^{-1} M_i'. \tag{A8}
\]
where $R_i^{-1}$ is the inverse matrix of $R_i$. The equation of motion of the sublattice moments in the new coordinate can be written as
\[
\frac{\partial \mathbf{M}'_i}{\partial t} = \gamma R_i[(R_i^{-1} \mathbf{M}'_i) \times (R_i^{-1} \mathbf{H}')].
\] (A9)
where $\mathbf{H}'_i = R_i \mathbf{H}_i$. Expressing Eq. (A9) with the matrix, we have
\[
\left(\begin{array}{c}
\frac{\partial M_1'}{\partial t} \\
\frac{\partial M_2'}{\partial t} \\
\frac{\partial M_3'}{\partial t} \\
\frac{\partial M_4'}{\partial t} \\
\frac{\partial M_5'}{\partial t} \\
\frac{\partial M_6'}{\partial t}
\end{array}\right) = \mathbf{M} = \left(\begin{array}{cccc}
M_1 & M_2 & M_3 & M_4 \\
M_5 & M_6 & M_7 & M_8 \\
M_9 & M_{10} & M_{11} & M_{12} \\
M_{13} & M_{14} & M_{15} & M_{16} \\
M_{17} & M_{18} & M_{19} & M_{20} \\
M_{21} & M_{22} & M_{23} & M_{24}
\end{array}\right)
\] (A10)
where
\[
\mathbf{\tilde{M}} = \left(\begin{array}{cc}
\tilde{M}_{xy} & \tilde{M}_{yz} \\
\tilde{M}_{zy} & \tilde{M}_{zz}
\end{array}\right).
\] (A11)
Here,
\[
\tilde{M}_{xy} = \left(\begin{array}{cccc}
0 & -\alpha & \alpha & 0 & \beta & -\beta \\
-\alpha & 0 & -\alpha & 0 & -\beta & \beta \\
0 & \beta' & -\beta' & 0 & \alpha_2 & -\alpha_2 \\
-\beta' & 0 & \beta' & 0 & \alpha_2 & \alpha_2 \\
\beta' & -\beta' & 0 & \alpha_2 & \alpha_2 & 0
\end{array}\right),
\] (A12)
\[
\alpha = \frac{M_0}{2} \{d_{tp} \cos \eta_1 + (\sqrt{3}A - d_{tc}) \sin \eta_1\},
\] (A13)
\[
\alpha_2 = \frac{M_0}{2} \{d_{tp} \cos \eta_2 + (\sqrt{3}A + d_{tc}) \sin \eta_2\},
\] (A14)
\[
\beta = \frac{\sqrt{3}}{2} B M_0 \sin \eta_1.
\] (A15)
The $\beta'$ in Eq. (A12) is given by the following replacement:
\[
\eta_1 \leftrightarrow \eta_4,
\] (A16)
\[
\tilde{M}_{yz} = \left(\begin{array}{cccc}
\gamma & \delta & \delta & 0 & \epsilon & \epsilon \\
\delta & \gamma & \delta & \epsilon & 0 & \epsilon \\
\delta & \delta & \gamma & \epsilon & 0 & \epsilon \\
0 & \epsilon & \epsilon & \gamma_2 & \delta_2 & \delta_2 \\
\epsilon & 0 & \epsilon & \gamma_2 & \delta_2 & \delta_2 \\
\epsilon & \epsilon & 0 & \delta_2 & \delta_2 & \gamma_2
\end{array}\right),
\] (A17)
By substituting Eq. (4) into Eq. (A10), we have
\[
(\tilde{M} - i \omega/\gamma \mathbf{E}) = 0,
\] (A27)
where $\mathbf{E}$ is a unit matrix. Theoretical ESR resonance modes in model 1 correspond to the absolute eigenvalues of $\omega/\gamma$. We obtain the eigenvalues by solving this secular equation.
In the case of the model 2, the angles $\theta_n$ and $\eta_n$ are given by

$\theta_1 = \pi/2, \quad \theta_2 = 11\pi/6, \quad \theta_3 = 7\pi/6,$
$\eta_1 = \eta_2 = \eta_3.$  \hspace{1cm} (A28)

The following calculation process is essentially similar to that for the model 1. By substituting Eqs. (A2), (A4), and (A28) into Eq. (2), we have

$$
F = -3HM_0 \sin \eta_1 + \frac{3}{2} AM^2_0 (1 - 3 \cos 2\eta_1) \\
- \frac{3}{2} \sqrt{3} dt \rho M^2_0 \cos^2 \eta_1 - \frac{3}{2} \sqrt{3} dt \rho M^2_0 \sin 2\eta_1 \\
+ \frac{1}{2} BM^2_0 (1 - 3 \cos 2\eta_1).  \hspace{1cm} (A29)
$$

The angle $\eta_1$ is determined by $\partial F/\partial \eta_1 = 0$ numerically. The magnetization $M$ induced along the $c$ axis is expressed as

$$
M = 3M_0 \sin \eta_1,  \hspace{1cm} (A30)
$$

where $M_0 = (N/3) g \mu_B |S|. \text{ Theoretical ESR resonance modes for model 2 of the DM model correspond to the absolute eigenvalues for the following matrix:}$

$$
\vec{M}_{\text{above}} = 
\begin{pmatrix}
0 & -\alpha_{ab} & \alpha_{ab} & \gamma_{ab} & \beta_{ab} & \beta_{ab} \\
-\alpha_{ab} & 0 & \alpha_{ab} & \gamma_{ab} & \beta_{ab} & \beta_{ab} \\
-\alpha_{ab} & \alpha_{ab} & 0 & \beta_{ab} & \gamma_{ab} & \beta_{ab} \\
\epsilon_{ab} & \chi_{ab} & \chi_{ab} & 0 & -\alpha_{ab} & \alpha_{ab} \\
\chi_{ab} & \epsilon_{ab} & \chi_{ab} & \alpha_{ab} & 0 & -\alpha_{ab} \\
\chi_{ab} & \chi_{ab} & \epsilon_{ab} & -\alpha_{ab} & \alpha_{ab} & 0
\end{pmatrix}.  \hspace{1cm} (A31)
$$

where

$$
\alpha_{ab} = M_0 \frac{1}{2} \{-dt_p \cos \eta_1 + (\sqrt{3} A + \sqrt{3} B - dt_c) \sin \eta_1\},  \hspace{1cm} (A32)
$$

$$
\beta_{ab} = M_0 \frac{1}{4} \{A + B - \sqrt{3} dt_c + (3A + 3B + \sqrt{3} dt_p) \cos 2\eta_1 + 2\sqrt{3} dt_p \sin 2\eta_1\},  \hspace{1cm} (A33)
$$

$$
\gamma_{ab} = M_0 \{(A + B + \sqrt{3} dt_c) \cos^2 \eta_1 + \sqrt{3} dt_p \sin 2\eta_1 - 2(A + B) \sin^2 \eta_1 + H \sin \eta_1\},  \hspace{1cm} (A34)
$$

$$
\epsilon_{ab} = M_0 \left\{ (A + B - \sqrt{3} dt_c - (3A + 3B + \sqrt{3} dt_p) \cos 2\eta_1 - 2\sqrt{3} dt_p \sin 2\eta_1 - H \sin \eta_1 \right\}.  \hspace{1cm} (A34)
$$

We obtain the eigenvalues for the model 2 by solving this secular equation as well.

APPENDIX B

As shown in Sec. IV B, we analyzed experimental results by the CF model using a mean-field approximation as well as the DM model. In this case, we have to consider the new coordinate $x', y', z'$:

$$
\begin{pmatrix}
M'_{CF1}, M'_{CF1}, M'_{CF1}
\end{pmatrix} = R_{CF1} M_i,  \hspace{1cm} (B1)
$$

where

$$
R_{CF1} = \begin{pmatrix}
\cos \theta_{cf1} \cos \eta_{cf} & \sin \theta_{cf1} \cos \eta_{cf} & \sin \eta_{cf} \\
-\sin \theta_{cf1} & \cos \eta_{cf} & 0 \\
-\cos \theta_{cf1} \sin \eta_{cf} - \sin \theta_{cf1} \sin \eta_{cf} \cos \eta_{cf}
\end{pmatrix},  \hspace{1cm} (B2)
$$

$$
\begin{align*}
\theta_{cf1} &= 3\pi/2, \\
\theta_{cf2} &= 5\pi/6, \\
\theta_{cf3} &= 7\pi/6, \\
\eta_{cf} &= -20\pi/180 = -\pi/9.
\end{align*}  \hspace{1cm} (B3)
$$

By substituting Eqs. (A2), (A3), and (B1)–(B3) into Eq. (7), we have for the model 1

$$
F = -H(3M_0 \sin \eta_1 + 3M_0 \sin \eta_4) \\
+ \frac{3}{2} AM^2_0 (2 - 3 \sin 2\eta_1 - 3 \sin 2\eta_4) \\
+ BM^2_0 (3 \cos \eta_1 \cos \eta_4 + 6 \sin \eta_1 \sin \eta_4) \\
+ 3K^2 \sin^2 (\eta_1 - \eta_4),  \hspace{1cm} (B4)
$$

For the model 2, the free energy $F$ can be written as

$$
F = -3HM_0 \sin \eta_1 + \frac{3}{2} AM^2_0 (1 - 3 \cos 2\eta_1) \\
+ \frac{3}{2} BM^2_0 (1 - 3 \cos 2\eta_1) + 3K^2 \sin^2 (\eta_{cf} + \eta_1) \\
- 3C^2 \cos^2 (\eta_{cf} + \eta_1).  \hspace{1cm} (B5)
$$

We calculate theoretical ESR resonance modes for the CF model by an essentially similar method to Appendix A.

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