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Osaka University
Doctoral Thesis

High Field Magnetism of Two-Dimensional Frustrated Antiferromagnets

(2次元フラストレート反強磁性体の強磁場磁性)

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February, 2013
Abstract

Magnetic properties of frustrated antiferromagnets have been well investigated theoretically and experimentally, and various noble states such as a "spin liquid" and a "spin-nematic" state are expected to be realized. Especially, triangular-lattice antiferromagnets have been studied as one of the most typical frustrated antiferromagnets for many years, and 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.

These magnetic systems sensitively change their magnetic properties by some parameter such as temperature, magnetic field, and doping of other ions. Therefore, frustrated magnets have been subjected to extensive research for many years. In addition, noncollinear magnetic structures such as a spiral magnetic structure are realized in consequence of competition of the exchange interactions between magnetic ions. Magnetically driven ferroelectricity induced by such a spiral magnetic structure due to frustration have been paid attention as multiferroicity, and attracted considerable interest due to the possibility of their applications in recent years. Thus, research on frustrated spin systems attracts attention not only from fundamental physical properties but from a viewpoint of its application. There are, however, not many examples of frustrated spin systems with ideal lattices and single crystal forms. Recently, nearly ideal quasi two-dimensional (2D) frustrated antiferromagnets such as a triangular and a kagome-lattice antiferromagnets were synthesized owing to the development of synthesis techniques. Here, we focus on two compounds of the quasi 2D frustrated antiferromagnets: KFe$_3$(OH)$_6$(SO$_4$)$_2$ and CuFe$_{1-z}$Ga$_z$O$_2$, and investigate their magnetic properties in high magnetic fields of up to about 55 T.

KFe$_3$(OH)$_6$(SO$_4$)$_2$ (K-Fe-jarosite) has attracted a substantial interest as a candidate of a classical Heisenberg kagome lattice antiferromagnet. 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 due to lattice distortion, partial substitution of nonmagnetic ions, and considerably large amounts of impurities. These problematic points, by contrast, have not been reported on K-Fe-jarosite, and thus, this jarosite is regarded as one of the ideal frustrated spin systems. Moreover, high quality large single crystals of K-Fe-jarosite, which were made by recent development of the precipitation reaction method, enable us to investigate the details of kagome physics without any assumption. We have performed high-field multi-frequency 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$_4$)$_2$ in order to investigate the behavior of classical Heisenberg kagome lattice antiferromagnet. We have analyzed the magnetization curve and the ESR excitation modes for $H \parallel c$ (perpendicular to the kagome layers) 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, and determined the physical parameters precisely. These parameters also reproduce the experimental results for $H \perp c$. In addition, we have clarified the origin of a field-induced metamagnetic transition observed in the magnetization curve for $H \parallel c$. 

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CuFeO$_2$ has attracted a lot of attention as a large spin-lattice coupling system, a field-induced multiferroic, and so on. Since Fe$^{3+}$ ions with 3$d^5$ high-spin configuration have no orbital angular momentum, this is usually regarded as a Heisenberg-type spin system. CuFeO$_2$, however, exhibits a 4-sublattice (4SL) collinear order below 11 K at zero magnetic field. Moreover, several successive phase transitions take place well below 11 K, when the external field $H$ along the c-axis is increased. Above $H_{c1}$=7 T, ferroelectric and incommensurate spiral (FEIC) order (7 T < $H$ < 13 T) is realized, and then a five-sublattice (5SL) (13 T < $H$ < 20 T) order was observed. Also the changes of magnetic properties caused by substitution of nonmagnetic ions such as Al$^{3+}$ and Ga$^{3+}$ for Fe$^{3+}$ ions have been studied. Such substitution reduces $H_{c1}$ with increasing the concentration of nonmagnetic ions. This result indicates that the FEIC phase becomes stable and the realization of this phase can be controlled by substitution of nonmagnetic ions. We compared ESR results with the electric polarization and the magnetization to clarify the origin of expansion of the FEIC phase by doping of nonmagnetic Ga$^{3+}$ ions. We observed a rapid increase of the ESR line width and a large shift of the transition field $H_{c1}$ accompanied with a magnetization jump and a spontaneous electric polarization by slight doping of Ga$^{3+}$ ions. We have found that the ESR line-width is highly correlated with this shift. As a result, we have succeeded in explaining the origin of the expansion of the FEIC phase and also the change of the transition field by broadening of the lowest excitation branch with the increase of the content of Ga$^{3+}$ ions.
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1 Introduction

1.1 Frustrated spin systems

In search for unusual magnetic ground states and spin dynamics, frustrated spin systems have been main subjects of both theoretical and experimental investigations in recent years. In such systems, the frustration is generated by the competition of different kind of interaction and/or by the lattice geometry, and the ground state is highly degenerate. Various novel states are expected to be realized, and therefore frustrated magnetic systems have been recognized as “treasury of novel properties”.

The spin frustration is caused by two kinds of origins as mentioned above. One arises from the geometry of the lattice, and the other from the existence of further-neighbor interactions which compete with the nearest neighbor interactions. In the present thesis, we mainly focus on the former case which is named “geometrical frustration”. The competition can be induced by geometry of the lattice on the intersection points of which magnetic ions are arranged. First, we explain geometrical frustration by using Figs. 1. When ferromagnetic (FM) interactions work between nearest Ising spins on apices of a regular square, the spins align parallel to each other as shown in Fig. 1(a). For the case of antiferromagnetic (AFM) interactions, the spin arrangement is uniquely determined when putting an up-spin at the $S_1$ site as shown in Fig. 1 (b). In the case of a regular triangle, spins are oriented in the same direction [see Fig. 1 (c)] when the interactions are ferromagnetic. In all these cases, the ground state and its energy are determined unambiguously. On the contrary, when antiferromagnetic interactions work between the Ising spins on a regular triangle, the situation differs from the others. When $S_1$ and $S_2$ spins are arranged antiparallel, $S_3$ cannot arrange itself simultaneously antiparallel to both $S_1$ and $S_2$. Then, the $S_3$ feels frustration. Such a situation, where the optimization is not attained, is called geometrical frustration. Thus, in many geometrically frustrated spin systems, the triangular structure (geometry of the lattice) and antiferromagnetic nearest neighbor interactions play an important role, and a number of examples have been reported so far. In a lattice which is covered with regular triangles, the spin configuration can not be determined uniquely, and macroscopic degeneracy remains in the ground state. Then, conventional magnetic ordering tends to be destabilized, and the effect of large fluctuation appears in the frustrated spin systems. Such macroscopic degeneracy and fluctuations are expected to be the causes which brings about novel physical properties peculiar to the frustrated spin systems.

Chronologically speaking, frustrated spin systems were first investigated about six decades ago. The first example on a periodic lattice was the antiferromagnetic Ising model on a regular triangular-lattice with the nearest-neighbor exchange interactions by Wannier in 1950 [1]. Non collinear spiral spin configurations due to competing interactions were first discovered independently by Yoshimori [2], Villain [3], and Kaplan [4] in 1959. In 1973, a “spin liquid state”, so called resonating valence bond (RVB) state, was proposed by Anderson, and studies on spin frustration took this occasion to become active [5]. Extensive investigations on frustrated spin systems really started in 1977 by Toulouse [6] and Villain [7] in the context of spin glasses, where the word ”frustration” was first introduced to describe the situation in which a spin in the system cannot find any orientation to fully satisfy all the interactions with its neighboring
Figure 1: Simple example of geometrical frustration. Ising spins on the corners of a regular square and triangle. (a) ferromagnetic case on the square, (b) antiferromagnetic case on the square (c) ferromagnetic case on the triangle (d) antiferromagnetic case on the triangle. This case is one of the most simple examples of geometrical frustration. There are six spin configurations with the same energy.

spins.

The effects of frustration are rich and often unpredictable. Frustrated spin systems provide a rich variety of magnetic states, such as a spin liquid and a spin nematic state. On the other hand, in some cases, frustration brings about a complex long range order and an exotic ground state such as a "spin glass". Although there are many approaches to investigate such novel states, most mechanisms giving rise to the novel states have not been understood completely yet at present. Recent studies on frustrated spin systems show that many statistical methods and theories have encountered a number of difficulties in dealing with the frustration. For example, a quantum Monte Carlo (QMC) calculation has a so-called negative sign problem due to the frustration, and a density matrix renormalization group (DMRG) method is not valid because of two or three dimensionality in many lattices with geometrical frustration. Experimentally, most syntheses of ideal model compounds were reported to be difficult because of contamination of impurities, lattice defects, and lack of single crystals. Since many phenomena associated with spin frustration are not understood completely, it is desired to search good materials related to simple model systems.

In recent years, a "spin liquid state" described above has renewed interests of many researchers, because the number of model compounds showing no long range magnetic order down to a very low temperature increases gradually thanks to recent develop-
ments of synthesis techniques. Moreover, some of the frustrated systems with a spiral magnetic order exhibit a giant magnetoelectric (ME) effect [9], and thus they are called multiferroics. There has been a considerable number of researches on such multiferroics because of their potential of application to electronic devices. Hence, researches of spin frustration attract much attention not only from fundamental physical properties but from a viewpoint of their application.

1.2 Phenomena caused by spin frustration

Spin frustration causes various physical phenomena. Here, we raise some effects and phenomena caused by spin frustration.

1. Suppression of magnetic long range ordering

Generally, a three-dimensional system without spin frustration exhibits a magnetic long range order (LRO) at a temperature comparable to the exchange interaction. According to the mean field approximation, the magnetic long range order takes place at about the absolute Weiss temperature $|\Theta|$ or a temperature slightly lower than $|\Theta|$. On the other hand, magnetic LRO becomes suppressed to the temperature far below $|\Theta|$ under large spin frustration. A useful quality factor for gauging the effect of spin frustration is the frustration parameter,

$$f = |\Theta|/T_N,$$

where $T_N$ is the Néel temperature, namely observed ordering temperature. When the spin frustration in the system is strong, the frustration parameter $f$ becomes large.

In some situations, any magnetic long range order can not be observed down to extremely low temperatures. Such particular state is called a "spin liquid" state, and has been studied for many years.

2. Appearance of noncollinear magnetic structure

In classical frustrated XY and Heisenberg spin system, it is thought that their ground states show magnetic long range order. However, the systems do not exhibit a simple collinear magnetic order. For example, a noncollinear ordered state where the direction of neighboring spins differs by 120° becomes stable in a Heisenberg regular triangular lattice antiferromagnet. The so-called "120° spin structure" is shown in Fig. 2(a).

Furthermore, a noncollinear incommensurate magnetic structure is realized, when the competition between more complicated exchange interactions exists. Here, we consider the nearest-neighbor (NN) $J_1$ and the next nearest-neighbor (NNN) $J_2$ interactions on a one-dimensional (1D) spin system ($J_1$-$J_2$ model). The system becomes frustrated and exhibits an incommensurate spiral magnetic structure as shown in Fig. 2(b), when the NNN interaction is antiferromagnetic. Such a spiral spin structure is expected to play an important role in generating electric polarization.

3. Realization of novel states

According to the third law of thermodynamics, the entropy of a system becomes zero at absolute zero temperature. When a system, where a magnetic long range order is suppressed by spin frustration, is in the state with a finite magnetic entropy, it
must emit its entropy during the process toward absolute zero temperature. Some kind of order appeared in a frustrated spin system may largely differ from the order in a conventional magnetic system. For instance, Berezinskii, Kosterlitz and Thouless formulated a theory on a vortex-induced topological phase transition (KT transition) in a 2D XY model [10] as shown in Fig. 3(a). Additionally, the ground state of the XY model possesses a hidden Ising-like discrete degeneracy. Moreover, as mentioned in the previous section, the ground state of the $S=1/2$ triangular lattice antiferromagnet is expected to be an RVB state [5], where singlet bonds are formed everywhere and rearranged with fluctuations in space and time as shown in Fig. 3(b).

If we consider only nearest-neighbor exchange interactions on an XY triangular lattice antiferromagnet, the ground state shows the 120° spin structure, which is two-fold degenerate depending on whether the resulting non-collinear spin structure is right- or left-handed (chiral degeneracy) as shown in Figs. 4(b) and (c). To characterize these two chiral states, a chirality vector (see Fig. 4(a)) is defined on each upward triangle by

$$\kappa = \frac{2}{3\sqrt{3}}(S_1 \times S_2 + S_2 \times S_3 + S_3 \times S_1),$$

where the corner sites 1, 2 and 3 are numbered clockwise. Miyashita and Shiba showed that the “chiral order” (the ordering of the chirality vectors) occurs in the XY triangular lattice antiferromagnet by means of Monte Carlo simulations [11]. The entropy is decreased in frustrated spin system by the emergence of such vortex or chiral order.

4. Reduction of frustration by coupling with other degrees of freedom
Since the spin frustration is not settled by the spin degrees of freedom, some frustrated materials resolve their degeneracy through the coupling with other degrees of freedom, such as lattice, electrical charge or orbital. Here, we provide a simple example of a “spin-lattice coupling”. If a regular triangle is distorted as shown in Fig. 5, the exchange interactions between spins on the apices change their magnitudes. The exchange interaction between the extended bond becomes weak, while that between the contracted bond becomes strong. As a result, the arrangement of the spins is determined uniquely and this phenomenon is called a spin Jahn-Telle effect.

Figure 2: (a) 120° spin structure. (b) incommensurate spiral magnetic structure.
Figure 3: (a) KT-type vortex in an XY model. (b) short-correlated resonating valence bond (RVB) state.

Figure 4: (a) chirality vector. (b) right- and (c) left-handed non-collinear spin structure, each of which is characterized by the opposite chirality as shown by (+) and (-).

Figure 5: Reduction of spin frustration by lattice distortion.
1.3 Various frustrated magnetic systems

Various kinds of frustrated magnetic systems have been studied and synthesized, and some of them are shown in Figs. 6. These are categorized by their dimensionality, namely one-, two- and three-dimensionality. In most of the depicted systems, spin frustration is caused by their geometry formed by triangular units, and thus they are called geometrically frustrated magnetic systems. In contrast, spin frustration arises from the competition between the nearest neighbor and distant interactions. Such cases are depicted in Figs. 6(d) and (g). In this thesis, we mainly discuss two-dimensional (2D) geometrically frustrated antiferromagnets. Generally, a long range order is easy to take place, when the coordination number $z$ is large. The corner-sharing arrangement in the kagome lattice ($z = 4$) in Fig. 6(f) leads to stronger frustration than the edge-sharing arrangement in the triangular lattice ($z = 6$) in Fig. 6(e).

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Figure 6: Examples of frustrated magnetic systems. (a) delta chain, (b) zigzag chain, (c) triangular tube, (d) $J_1$-$J_2$ model, (e) triangular lattice, (f) kagome lattice, (g) honeycomb lattice with distant interaction $J_2$, (h) fcc lattice, and (i) pyrochlore lattice.
1.4 Purpose of this study

Magnetic properties of 2D geometrically frustrated antiferromagnets have been well investigated theoretically, and various novel states such as a spin liquid and a spin-nematic state are expected to be realized. There are, however, not many experimental examples corresponding to ideal 2D geometrically frustrated antiferromagnets. Especially, reports on the synthesis of high-quality single crystal samples are rare. Since frustrated spin systems are considered to be sensitive to impurities and lattice defects, high-quality single crystal samples are desired. The high-quality single crystal samples enable us to investigate physical properties in details without any assumption.

We have studied mainly two compounds of the 2D geometrically frustrated spin systems, namely, KFe$_3$(OH)$_6$(SO$_4$)$_2$ (K-Fe-jarosite) and CuFe$_{1-x}$Ga$_x$O$_2$ ($x=0.000\sim0.028$). As for the former compound, the synthesis of high-quality single crystal sample was reported quite recently. These compounds were reported to indicate interesting magnetic properties associated with the geometrical frustration written below.

$S = 5/2$ kagome lattice antiferromagnet KFe$_3$(OH)$_6$(SO$_4$)$_2$

K-Fe-jarosite has magnetic Fe$^{3+}$ (spin $S = 5/2$) ions which form kagome lattices in the $c$ plane, so that this jarosite can be identified as a two dimensional frustrated classical spin system. The K-Fe-jarosite remains undistorted down to sufficiently low temperatures. There are few previous experimental reports on single crystals of a classical kagome-lattice antiferromagnet. This study provides an in-depth study on a ideal classical Heisenberg kagome-lattice antiferromagnet using a single crystal. ESR and magnetization are useful for evaluating the perturbation parameters such as anisotropy constants which may dominantly affect the magnetic properties of this kagome lattice compound. Thus, we have performed magnetization and ESR measurements in magnetic fields of up to about 50 T with pulse magnets in order to discuss the origin of the anisotropy in K-Fe-jarosite.

$S = 5/2$ triangular lattice antiferromagnet CuFe$_{1-x}$Ga$_x$O$_2$

CuFeO$_2$ consists of triangular layers of Fe$^{3+}$ (3d$^5$) ions which are stacked perpendicularly to the [001] direction, so that CuFeO$_2$ can be identified as a two dimensional frustrated classical spin system. CuFeO$_2$ has yielded unanticipated properties by frustration and the spin-lattice coupling, and indicates unusual magnetic long orderings. Additionally, CuFeO$_2$ has attracted a renewed interest as one of the multiferroic materials since the occurrence of a spontaneous electric polarization was reported in the field induced phase (ferroelectric and incommensurate phase). Furthermore, fascinating physical properties were also observed when the magnetic Fe$^{3+}$ ions were replaced by tiny amounts of non-magnetic ions. The ferroelectric and incommensurate(FEIC) phase can be induced at zero magnetic field by a certain amount of nonmagnetic ions. This result indicates that the ferroelectric phase becomes stable and this phase can be expanded by the substitution of nonmagnetic ions. However, the origin of the expansion of the FEIC state by doping of nonmagnetic ions is still unclear. Therefore, we investigate the behavior of Ga$^{3+}$ doped CuFeO$_2$ in high magnetic fields. ESR is one of the most powerful techniques to study magnetic excitations with high reso-
lution. Moreover, we can study the change of the physical parameters such as exchange constant and anisotropy constants by doping of nonmagnetic ions in detail. Accordingly, we performed multi-frequency ESR measurements to clarify the reason why the transition field to FEIC state shifts largely with increasing $x$ in CuFe$_{1-x}$Ga$_x$O$_2$.

This thesis is organized as follows; In section 2, we show experimental apparatus. In sections 3 and 4, we explain the experimental and analytical results on single crystals of KFe$_3$(OH)$_6$(SO$_4$)$_2$ and CuFe$_{1-x}$Ga$_x$O$_2$. Final section is devoted to the summary.
2 Experimental

We carried out ESR measurements using pulsed and static magnetic field system. The choice of the measurement system depends on the range of the measurement frequency and the magnetic fields. Our ESR measurement system composed of a vector network analyzer and a superconducting magnet was used in static magnetic fields of up to 14 T for the frequencies below 630 GHz. Pulsed field ESR measurements were conducted in magnetic fields \((H)\) of up to 53 T by using our pulsed field ESR apparatus equipped with a non-destructive pulse magnet, a far-infrared laser, several kinds of Gunn Oscillators which cover the frequency range between 75 GHz and 2 THz. High-field magnetization measurements were performed in pulsed magnetic fields of up to 53 T. Electric polarization \(P\) was measured in pulsed magnetic fields of up to 22 T.

2.1 ESR measurement system in static magnetic fields

![Figure 7: (a) Block diagram of ESR measurement system in static magnetic fields, which is composed of a vector network analyzer and a 16 T superconducting magnet. Sample setting for (b) faraday and (c) voigt configuration.](image)

Figure 7(a) shows the block diagram of the ESR measurement system in static magnetic fields. We use a 16 T superconducting magnet (Oxford Instruments, UK), and the magnetic field can be swept up to 14 T when the magnet is cooled down to 4.2 K by liquid He. An insert (variable temperature insert: VTI) is used to change the temperature of the sample space from 1.4 K to 300 K. The temperature of the sample is measured by using a calibrated cernox resister thermometer placed close to the sample and is controlled by a heater of Manganin-wire. We use a vector network analyzer (MVNA-8-350, AB Millimeter, France) with high frequency ESA-1 and ESA-2 extensions. The Gunn Oscillator A of ESA-1 sends its emitted microwave frequencies \(F_a\) into the Schottky multiplier (SM). Non-linear effects due to the Schottky diode create harmonic frequencies \(M \times F_a\) (\(M\): integer), and one of these harmonics is selected for
the experiments. At the same time, the Gunn Oscillator B of ESA-2 sends its emitted microwave frequencies \( F_b \) into the the Schottky Harmonic Mixer (SHM), which also creates harmonic frequencies \( M \times F_b \) (\( M: \) integer). Then we detect the difference frequency \( M \times (F_a - F_b) \), which can easily be extracted and amplified. Microwaves are introduced into the sample in a cryostat which is made of light pipes with the diameter of 8 mm. We observe not only the amplitude but also the phase of the ESR signals with this vector network analyzer so that we can determine the resonance field precisely even though the shape of the signal deformed by mixing the dispersive component into the absorbing one of the ESR signal. A thin stainless steel jacket is used to avoid the noise from a bubbling of liquid helium. The microwaves for the frequency from about 30 GHz to about 700 GHz can be generated almost continuously. We can observe ESR spectra for two different frequencies at the same time (dual frequency potion).
2.2 ESR measurement system in pulsed magnetic fields

Figure 8 (a) shows the block diagram of the ESR measurement system in pulsed magnetic fields. As well as the static field ESR system, we can use both faraday [Figure 8 (b)] and voigt configuration [Figure 8 (c)], and the choice of the setting depends on the shape and the crystallographic directions of the sample. Submillimeter waves at frequencies from about 500 GHz to about 2.0 THz are generated with a FIR laser (Edinburgh Instruments, UK), which is excited by a CO₂ pumping laser and produces many different frequencies by changing molecular gases such as a methanol, and those at frequencies below 500 GHz are obtained by using several Gunn-oscillators with doubler (75, 90, 110, 130, 150, 180, 220, 260 GHz) and backward wave oscillator (BWO) (250 ~ 500 GHz). ESR signals are detected with an InSb hot electron bolometer (QMC instruments Ltd.) which is magnetically tuned to offer optimized sensitivity over the maximum possible range of frequencies between millimeter and sub-millimeter wavelengths. The temperature of the sample is measured by using a thermocouple (pair of Au + 0.07 % Fe and Ag) placed close to the sample. The measurements at low temperatures down to 1.3 K were performed by pumping liquid ³He.

We employed nondestructive short pulsed magnets with the duration time of ~ 7 msec for ESR measurements. The pulse magnet is made by winding with a Cu-Ag wire of high-tensile strength (cross-section area: 2 × 3 mm², tension strength: 900 MPa) and reinforced by a maraging steel cylinder as shown in Fig. 9(a). The diameter of the bore of this magnet is 18 mm. To prevent the damage of Joule heating accompanied by generating a magnetic field, it is cooled down using surrounding liquid N₂ (see Fig. 8). The magnet is driven by the capacitor bank system as shown in Fig.10. The magnet current is supplied sinusoidally by the capacitor bank, which can store charge energy of up to 1.5 MJ (20kV, 7.5 mF), through a discharge of air gap type of switch (start...
switch in Fig. 10. After a half of the period, the current is dumped into the crowbar circuit using a crowbar switch in Fig. 10 in order to avoid an additional Joule heating of the magnet. We can produce a pulsed magnetic field of up to about 55 T. The shape of the pulsed magnetic field are shown in Fig. 9(b). We can control the duration time by changing the number of the capacitor banks (at most six banks) as shown in Fig. 10. The duration time is proportional to $\sqrt{LC}$, where $L$ and $C$ are the inductance of the pulse magnet and the capacitance of the capacitor banks, respectively.

Figure 9: (a) Schematic cut view of a pulse magnet. The magnet is held by stainless steel flanges. (b) Shapes of a pulsed magnetic field produced by using six banks with 7 kV, five banks with 6 kV, four banks with 8.5 kV, four banks with 4 kV, three banks with 3 kV, two banks with 3 kV, and one bank with 2 kV, respectively.

Figure 10: Schematic view of the circuit of the capacitor bank system.
2.3 Magnetization measurement system in pulsed magnetic fields

Figure 11(a) shows the block diagram of the high-field magnetization measurement system in pulsed magnetic fields. The pulse magnet is the same type as for ESR measurement. The magnetization is measured by using a balanced pick-up coil system. The technique of reducing the background flux change due to a transient field, which is usually $10^4$~$10^6$ times larger than the flux change caused by the magnetization of the specimen, is shown schematically in Fig. 11(b). The A-coil picks up the magnetic flux changes and the external field while the B-coil is wound oppositely to the A-coil in order to compensate the background flux change. A fine adjustment is established with the one turn C-coil. Considering the field duration and frequency response, the A-coil is wound with 80 turns on a 3.0 mm diameter bakelite pipe. The B-coil is wound with 40 turns coaxially on the A-coil on a 4.3 mm diameter in opposite direction to the A-coil. The C-coil is wound with one turn coaxially on the others. The cross section of the B-coil is twice as large as that of the A-coil so as to receive the same amount of external flux in the two coils. In this way, we can obtain only an induced voltage coming only from a magnetization of the sample. We obtain the magnetization signals as $dM/dt$. The field and magnetization pick-up coils were calibrated by a single crystal of MnF$_2$ as the standard specimen using the known values of the spin-flop transition field and the slope of the magnetization above the transition. The measurements at low temperatures down to 1.3 K were performed by pumping liquid $^4$He.

Figure 11: (a) Block diagram of pulsed field magnetization measurement system. (b) Cut view of a co-axial type pick-up coil system.

In addition, we carried out the magnetization measurements below 7 T to calibrate the magnetization values with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL7).
2.4 Electric polarization measurement system in pulsed magnetic fields

Figure 12 shows the block diagram of high-field electric polarization measurement system in pulsed magnetic fields. We have developed our electric polarization apparatus by referring to the works by Mitamura et al. [12, 13], and use a pyroelectric technique. Figure 13(a) shows the schematic circuit for the electric polarization measurements in pulsed magnetic fields. We prepared plate-shaped samples, and the electrodes were formed by the silver paste on both sides of the largest flat surfaces [Fig. 13(b)]. When the spontaneous polarization $P$ is produced in the sample, electric charge $Q$ appears on the electrodes. The pyroelectric current $I_p$ then flows as indicated in the figure until the potential difference across the electrodes becomes equal to that of the voltage source $V_p$. $P - I_p$ relation is given by $dP/dt = 1/S \cdot dQ/dt = I_p/S$, where $S$ is cross-section area of the sample. The electric polarization $P$ is obtained by integrating the pyroelectric current $I_p$ against the time,

$$P = \frac{1}{S} \int I_p \, dt. \quad (3)$$

This pyroelectric current can be measured as a voltage across the shunt resistor $R_s$. We used a 10 kΩ standard resistance as $R_s$, which is considered to be much smaller than the internal resistance of the sample. The voltage source in Fig. 13(a) provides a poling field $E_p$ on the sample to align the ferroelectric domains. We applied the voltage $V_p$ of ~90 V with a source meter (Keithley Instruments).

![Block diagram of the pulsed field electric polarization measurement system.](image)

We utilized a long pulse magnet which generates a pulsed magnetic field of up to 55 T with the field duration of ~30 msec, because a slow field-sweep rate makes the signal of electric polarization large. For this long pulse magnet, we use another capacitor bank with the capacitance of 11.0 mF. The shape of the pulsed magnetic field are shown with different charge voltages in Fig. 14.
Figure 13: (a) Schematic circuit of pulsed field electric polarization measurement system (b) details of the sample setting at the probe of the electric polarization measurement

Figure 14: Shapes of a pulsed magnetic field with different charge voltages for electric polarization measurements
3 $S=5/2$ kagome-lattice antiferromagnet

$KFe_3(OH)_6(SO_4)_2$

3.1 Introduction

3.1.1 Classical kagome lattice antiferromagnet

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. For the quantum case, the Heisenberg antiferromagnet with the smallest spin value $S=1/2$ on a 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. Here, on the contrary, we study the classical case, namely the Heisenberg antiferromagnet with a large spin value.

Figure 15 shows possible ground states of the classical kagome-lattice antiferromagnet. The ground states satisfy 120° spin structure, in which the angle between the nearest pair of spins is 120°, and is expected to possess three possible spin structures, two different $q = 0$ and one $q = \sqrt{3} \times \sqrt{3}$ structures. Figures 1(a) and 1(b) show $q = 0$ spin structure with positive and negative chirality, respectively. The positive (negative) chirality is defined as clockwise (counterclockwise) spin rotation in the view of clockwise spin-site rotation as already mentioned in § 1. Figure 1(c) shows the $q = \sqrt{3} \times \sqrt{3}$ spin structure which has triangles with both positive and negative chirality. From the spin configurations shown in Fig. 15, the classical ground state has a continuous degeneracy due to the “weathervane” rotation of the spins as indicated by ellipsoids with an arrow, and thus no long range order is expected even at zero temperature [15, 16, 17, 18].

![Figure 15: (a), (b) $q = 0$ spin structures. (c) $q = \sqrt{3} \times \sqrt{3}$ spin structure.](image)
3.1.2 Classical kagome lattice antiferromagnet with Dzyaloshinsky-Moriya (DM) interaction

In frustrated spin systems, it is expected that any small perturbation may have a strong effect on the ground-state manifold. It has been 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 [14]. Moreover, in real systems, there are small perturbations such as next-nearest interactions, interlayer interactions, anisotropies, or defects. These small perturbations determine spin structure in most situations. For example, when the NNN interaction is ferromagnetic (antiferromagnetic), \( J_2 < 0 \) \((J_2 > 0)\), the ground state has the \( q = \sqrt{3} \times \sqrt{3} \) \((q = 0)\) spin structure. This section focuses on the Dzyaloshinsky-Moriya (DM) interaction, because this interaction is inevitable in a kagome lattice where no inversion symmetry exists between neighboring magnetic sites. The DM interaction between the neighboring \( i \)- and \( j \)-site spins is defined using the DM vector \( \mathbf{d}_{ij} \),

\[
\mathbf{d}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j. 
\]  

Moriya clarified the conditions for the existence of the DM interactions, and gave some rules for the determination of the possible directions of \( \mathbf{d}_{ij} \) [19]. He proposed a microscopic derivation of these interactions based on Anderson’s formalism of superexchange interaction, including the spin-orbit coupling. In some antiferromagnets, the DM interaction is responsible for weak ferromagnetism. Elhajal et al. [20] investigated a Heisenberg kagome-lattice antiferromagnet with the DM interaction in detail by a mean field approximation and a classical Monté Carlo simulation. In their paper, two components of the DM interaction are treated separately, namely \( d_z \) : the \( z \) component parallel to kagome plane and \( d_p \) : the in-plane component perpendicular to the \((i j)\) bond \((z\) is the axis perpendicular to the kagome plane\.). They argued that the \( d_z \) acts to create an easy-plane anisotropy.

According to their calculations [20], we first describe the case of \( d_{ij} \perp \) kagome plane and thus the component of the DM vector is only \( d_z \). The coplanar magnetic structure is realized, and the direction of the chirality vector is determined by the sign of \( d_z \). Accordingly, \( d_z > 0 \) and \( d_z < 0 \) stabilize \( q = 0 \) structure with positive and negative chirality, respectively, as shown in Fig. 16(a). The transition temperature \( T_c \) between the disordered and the LRO states as a function of \( d_z/J \) is plotted in Fig. 16(b). At \( d_z/J = 0 \), no long range order is expected as mentioned above. However, as soon as \( d_z/J \) has a finite value, even much smaller than \( J \), a phase transition occurs at a finite temperature. Owing to this effect of the DM interaction, the low-temperature magnetic structure can be determined.
Figure 16: (a) Spin configuration in the kagome plane determined by $d_z$, and its sign chooses the chirality. (b) Transition temperature $T_c$ as a function of $d_z/J$ for $d_{ij \perp}$ kagome plane [20].
Figure 17: In-plane DM component represented at the middle point between the magnetic sites with open arrows and the associated magnetic structure indicated by solid arrows. All the spins have a weak z component, resulting in weak ferromagnetism [20].

Next, we discuss the case of the DM vector parallel to kagome plane $d_p$ ($d_{ij}$||kagome plane). The $d_p$ vectors as well as the ground state magnetic configuration obtained by the mean field approximation and Monte Carlo simulations are depicted in Fig. 17. The structure has some similarities with the $d_z>0$ case for $d_{ij}$||kagome plane, and indeed it has the positive chirality. However, the spins do not lie in the kagome plane anymore, but they all have the same out of plane z component, giving rise to weak ferromagnetism, perpendicular to the kagome plane. The so-called umbrella spin structure as shown in Fig. 17 becomes stable. Each spin points towards a fixed direction. In this case, the DM interaction seems to act more similar to an easy-axis anisotropy. The canting angle $\eta$ depends on $d_p/J$. This angle, as well as the weak ferromagnetic component, increases with $d_p/J$.

Finally, we turn to the general case where $d_{ij}$ lies in the plane perpendicular to the $i$-$j$ bond ($d_{ij}$⊥$i$-$j$ bond. Both $d_p$ and $d_z$ are present. ). Figure 18 shows the ground state obtained for different values of $d_p$ and $d_z$ divided by $J$ (in-plane and out-of-plane components of $d_{ij}$). If $d_z>0$, the positive chirality is selected and this is the same effect as that coming from the in-plane component $d_p$. All the spins have a finite z component when $d_p$ is non-zero and $d_z>0$. The case $d_z<0$ is more complicated: the chirality favored by $d_z<0$ is not the same as the one which is selected if only the in-plane component $d_p$ is considered. When $d_{ij}$ is almost in the kagome plane with a small negative component along the z axis, the canted structure is selected with a ferromagnetic moment. There is a critical value of $d_z/d_p$, and if $d_z$ is negative enough, then the ground state is no longer the canted structure, but the $q=0$ spin structure with negative chirality. When a positive chirality and $d_p \neq 0$ are selected, the spins have an out-of-plane component with the angle $\eta$ between the spin direction and the
kagome plane given by,

$$\tan 2\eta = \frac{2d_p}{(\sqrt{3}J + d_z)}.$$  \tag{5}  

Figure 18: Ground state obtained for different values of $d_p$ and $d_z$ divided by $J$ (in-plane and out-of-plane components of $d_{ij}$). The gradation of the gray color represents the magnitude of $\eta$, the angle between the spin direction and the kagome plane. $\eta = 0$ corresponds to a structure where the spins lie in the kagome plane with zero out-of-plane component, $S_z = 0$. This is represented by the homogeneous gray color in the left part of the figure which is the same as on a dashed line in the right part. For the weak ferromagnetic structures with an out-of-plane magnetic component, $S_z \neq 0$, the gradation of white (black) color is proportional to the magnitude of positive (negative) value of $\eta$ \cite{20}.  

(a) Weak ferromagnetism \perp \text{kagome plane}  

(b) Coplanar structure  

Figure 18: Ground state obtained for different values of $d_p$ and $d_z$ divided by $J$ (in-plane and out-of-plane components of $d_{ij}$). The gradation of the gray color represents the magnitude of $\eta$, the angle between the spin direction and the kagome plane. $\eta = 0$ corresponds to a structure where the spins lie in the kagome plane with zero out-of-plane component, $S_z = 0$. This is represented by the homogeneous gray color in the left part of the figure which is the same as on a dashed line in the right part. For the weak ferromagnetic structures with an out-of-plane magnetic component, $S_z \neq 0$, the gradation of white (black) color is proportional to the magnitude of positive (negative) value of $\eta$ \cite{20}.  

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3.1.3 Experimental approaches

The number of reported experimental studies on 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 [Cu₃(titmb)₂(OOCCH₃)₆]·H₂O [21], herbertsmithite ZnCu₃(OH)₆Cl₂ [22, 23, 24, 25], volbosite Cu₃V₂O₇(OH)₂·2H₂O [26, 27], vesignieite BaCu₃V₂O₈(OH)₂ [28, 29] and A₂Cu₃SnF₁₂ (A=Rb, Cs) [30, 31, 32], 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. Expected results by theories for the S=1/2 kagome lattice antiferromagnet, e.g. spin liquid state, have not been obtained. Therefore, syntheses of compounds for the ideal kagome-lattice antiferromagnet are desired.

By constrast with these kagome-lattice antiferromagnets, Jarosites, which have a chemical formula AM₃(OH)₆(SO₄)₂ [33] 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⁺, NH₄⁺, H₃O⁺) and M³⁺(Fe³⁺, Cr³⁺, V³⁺, Al³⁺, Ga³⁺, In³⁺) ions. Here, we describe magnetic properties of Fe³⁺, Cr³⁺ and V³⁺ jarosite compounds. In Table 1, the comparison of the jarosite compounds is summarized.

<table>
<thead>
<tr>
<th>M³⁺</th>
<th>A⁺</th>
<th>TN, Tc, Tg (K)</th>
<th>Θ (K)</th>
<th>Experiments</th>
</tr>
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<tbody>
<tr>
<td>Fe³⁺</td>
<td>K⁺</td>
<td>TN = 65.4</td>
<td>-800</td>
<td>χ, M, C [34], NMR [35]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TN = 64.5</td>
<td>-829</td>
<td>EPNS [36], INS [37]</td>
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<tr>
<td></td>
<td>Rb⁺</td>
<td>TN = 63.4</td>
<td>-838</td>
<td>χ [33]</td>
</tr>
<tr>
<td></td>
<td>Ti⁺</td>
<td>TN = 61.5</td>
<td>-825</td>
<td>χ [33], NMR [38], EPNS [39]</td>
</tr>
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<td></td>
<td>Na⁺</td>
<td>TN = 59.5</td>
<td>-798</td>
<td>χ [40]</td>
</tr>
<tr>
<td></td>
<td>0.5Pb²⁺</td>
<td>TN = 56.4</td>
<td>-818</td>
<td>χ [33]</td>
</tr>
<tr>
<td></td>
<td>H₃O⁺</td>
<td>Tg = 13.8 ~17.5</td>
<td>-700</td>
<td>χ, C, INS [41, 42], μSR [43]</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>K⁺</td>
<td>TN = 4.1</td>
<td>-49</td>
<td>χ, M [44] [45], EPNS [46]</td>
</tr>
<tr>
<td></td>
<td>Rb⁺</td>
<td>TN = 4.2</td>
<td>-53</td>
<td>χ, M [44]</td>
</tr>
<tr>
<td></td>
<td>Na⁺</td>
<td>TN = 3.6</td>
<td>-39</td>
<td>χ, M [44]</td>
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<tr>
<td></td>
<td>NH₄⁺</td>
<td>TN = 8.1</td>
<td>-52</td>
<td>χ, M [44]</td>
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<tr>
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<td>K⁺</td>
<td>TC = 31.0</td>
<td>+54</td>
<td>χ, M [47],</td>
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<td>TC = 30.0</td>
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<td>χ, M [47]</td>
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<td>+54</td>
<td>χ, M [47], NMR [48], EPNS [49]</td>
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<tr>
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<td>NH₄⁺</td>
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<td>+53</td>
<td>χ, M [47]</td>
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</tbody>
</table>

χ: susceptibility, M: magnetization, C: specific heat
EPNS: elastic powder neutron scattering, INS: inelastic neutron scattering
*spin-glass behavior
Iron jarosites

The iron jarosites are strongly frustrated owing to a very pronounced intralayer antiferromagnetic exchange interaction (\( \Theta \sim -800 \text{ K} \)) [50]. All the stoichiometrically pure iron jarosites exhibit a LRO at finite temperatures. The magnetic behavior of alkali metal ion members of the jarosite series is characterized by a prominent Neel transition at \( T_N \sim 65 \text{ K} \) [50]. The cusp in the AC magnetic susceptibility is frequency-independent, indicating the absence of spin-glass behavior.

However, the LRO is absent in hydronium jarosite. In reaction process of hydronium jarosite, \((\text{H}_3\text{O})_{1-x} (\text{H}_2\text{O})_x \text{Fe}_3(\text{OH})_6(\text{SO}_4)_2\) and \((\text{H}_3\text{O})\text{Fe}_{3-x}(\text{H}_2\text{O})_{3x}(\text{OH})_{6-3x}(\text{SO}_4)_2\) are formed by the acid-base reaction between \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) and protonation of \( \text{OH}^- \) by \( \text{H}^+ \). The protonation of the hydronium jarosite lead to a decrease in the nearest neighbor exchange constant and consequently to depress \( T_N \). Since structural disorder is capable of inducing spin-glass behavior, the spin-glass-like properties of \((\text{H}_3\text{O})\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2\) are due to structural and attendant magnetic disorder caused by proton-transfer reactions.

Chromium jarosites

Chromium jarosites have the Weiss temperatures of \( \Theta \sim -50 \text{ K} \) [44]. The negative value \( \Theta \) indicates that the nearest-neighbor interaction is antiferromagnetic. The frustration parameter \( |\Theta|/T_N \) of the Cr-jarosites are comparably large to Fe-jarosite (6.4~13.3) [44]. Neutron diffraction studies on K-Cr-jarosite show that the magnetic structure in the ordered phase is the \( q = 0, 120^\circ \) spin structure in the kagome planes [see Fig. 19(a)] [46].

All the samples exhibit hysteresis loops below \( T_N \), which suggests magnetic ordering with small canted moments [44]. Figure 19(b) shows magnetization curves of \( \text{KCr}_3(\text{OH})_6(\text{SO}_4)_2 \) near zero field [45]. The ordered Cr moments are also considered to be canted slightly from the kagome plane. The weak ferromagnetic component on neighboring planes in the Cr-jarosites are parallel to each other [see the inset of Fig. 19(b)], and therefore the total moment throughout the whole sample is not zero.

Figures 19(c) and (d) show the high-field magnetization curves up to 50 T measured with a pulse magnet at 4.2 K and 1.3 K [45]. The magnetization curve for in-plane fields [Figs. 19(c)] exhibits anomalous undulation. They are more remarkable in the \( \text{d}M/\text{d}B \) curves, which indicate a sharp dip at 22 T. The magnetization at the inflection point is 1.2\( \mu_B \) per Cr atom, roughly close to 1/3 of the saturation magnetization. The dips are more pronounced at 4.2K than at 1.3 K. The slopes of the magnetization curves seem to decrease above 40 T. On the other hand, the magnetization in magnetic fields along the c-axis is simply proportional to applied fields [Fig. 19(d)]. On the basis of a classical model, Zhitomirsky simulated the magnetization as a function of magnetic field [51]. The calculation demonstrates that a ferrimagnetic up-up-down(\( \uparrow\uparrow\downarrow \)) spin structure is stabilized in magnetic fields below a certain temperature. However, the region of the 1/3 plateau becomes narrower with decreasing temperature in the lowest-temperature range. This proves that thermal fluctuations stabilize the ferrimagnetic order. This result is qualitatively consistent with the experimental observation.
Figure 19: (a) Magnetic structure of K-Cr-jarosite proposed by neutron diffraction studies below $T_N$ [46]. (b) Anisotropy in the magnetization curves of Cr-jarosite measured at $T = 1.8$ K. A weak ferromagnetism appears only for magnetic fields along the c-axis. The inset indicate a model of magnetic structure. High-field magnetization curves of Cr-jarosite in (c) in-plane and (d) out-of-plane magnetic fields. The insets show the field derivative of the magnetization $dM/dB$. 
Vanadium jarosites
The Weiss temperature $\Theta \sim +50$ K establishes the presence of the ferromagnetic nearest-neighbor interaction in Vanadium jarosites [47]. Since the nearest neighbor interaction is ferromagnetic, the spins are not frustrated. Ferromagnetic long range ordering was observed below the Curie temperature, $T_c \sim 30$ K. To determine the magnetic structure, neutron powder diffraction measurements on Na-V-jarosite were performed at 16 K [49]. Below $T_c$, the spins of $V^{3+}$ ions order ferromagnetically within each layer, and the ferromagnetically aligned layers stack antiferromagnetically as shown in Fig. 20(a). Figure 20(b) shows magnetization curves for a small crystal in external magnetic fields applied parallel and perpendicular of the c-axis. When the field is applied parallel to the c axis ($H||c$), the magnetization increases linearly with field strength, but it does not saturate at $H \sim 50$ kOe. The $V^{3+}$ single-ion anisotropy confines the exchange-coupled moments to lie within the kagome plane, thereby hardening the out-of-plane motion. Conversely, when the field is applied orthogonal to the hard axis ($H \perp c$), the magnetization increases abruptly and attains a limiting value when $H$ is in excess of 10 kOe.

Figure 20: (a) Magnetic structure of Na-V-jarosite proposed by neutron diffraction studies below $T_c$ [49]. (b) Magnetization vs $H$ plot of a Na-V-jarosite single crystal for $H||c$ and $H \perp c$ [47].

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 classical Heisenberg kagome-lattice antiferromagnets. In this thesis, we provides the experimental results of high field studies and the details of analyses in order to investigate which perturbation affects on this ideal classical Heisenberg kagome-lattice antiferromagnet.
3.2 Physical properties of KFe₃(OH)₆(SO₄)₂

3.2.1 Sample preparation and crystal structure

A single crystal sample (~2×2×0.5 mm³) of K-Fe-jarosite used in this study [see Fig. 21(b)] was prepared by a redox-based hydrothermal method [see Fig. 21(a)]. This sample was provided by one of the collaborators, K. Matan at Mahidol University. The details of the single crystal synthesis were reported in Refs. [50, 34]. Until recently, jarosites have been prepared typically by precipitation under hydrothermal conditions,

$$3\text{Fe}^{3+} + 2\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow \text{KFe}_3(\text{OH})_6(\text{SO}_4)_2 + 3\text{K}^+ + 6\text{H}^+. \quad (6)$$

Under these conditions, the monovalent K⁺ cation is susceptible to replacement by hydronium ions and the coverage of the Fe³⁺ lattice sites is incomplete. Also, only microcrystalline materials are obtained owing to the heightened acidity of the solution as well as the speed and intractability of the precipitation reaction. The challenges confronting the synthesis of pure jarosites have been overcome with the development of redox-based hydrothermal methods. Control over the precipitation of the jarosite is achieved by inserting two oxidation and reduction steps before reaction (6),

$$\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2, \quad (7)$$

$$2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}. \quad (8)$$

In this manner, the Fe³⁺ is slowly generated throughout the course of the hydrothermal process and the pH is moderated because three overall equivalents of protons are consumed in the production of an equivalent of jarosite. The hydrothermal vessel shown in Fig. 21(b) placed into a Fisher Isotemp oven with forced-air circulation set at 250°C. After 2 hours, the oven temperature was lowered to 220°C, and after another 2 hours was again lowered to 205°C. After 4 days at 205°C, the oven was cooled at a rate of
0.4°C /min. The reaction is performed at pH=1 to 1.5. The high quality large single crystals of K-Fe-jarosite enable us to investigate the details of the physics for an ideal classical kagome-lattice antiferromagnet without any assumption.

The K-Fe-jarosite belongs to a rhombohedral system with \( R\overline{3}m \) symmetry, and lattice constants are \( a=b=7.30 \ \text{Å} \) and \( c=17.09 \ \text{Å} \) at room temperature [52]. The crystal structure consists of kagome layers of Fe\(^{3+} \) ions with an electronic configuration \( t_{2g}^2e_g^2 \) in the \( ab \) plane. These planes stack along the \( c \)-axis, separated by nonmagnetic layers of \( \text{SO}_4^{2-} \) and \( \text{K}^+ \), as shown in Fig. 22(a). Neither the lattice distortion of the kagome plane nor the partial substitution of nonmagnetic ions have been reported and thus, this jarosite is regarded as one of the ideal frustrated spin systems. As depicted in Fig. 20 (b), the Fe\(^{3+} \) ions are coordinated with two oxygen atoms from \( \text{SO}_4^{2+} \) and four oxygen atoms from \( \text{OH}^- \) 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 22(c) and (d) indicate two types of arrangements of FeO\(_6\) octahedron in this compound. The tilting directions of the octahedron on each triangle against the \( c \)-axis change alternatively with the layers along the \( c \)-axis. The principal axis is tilted from the \( c \)-axis about \( \eta_{cf} = 20^\circ \).

Figure 22: (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 \( \text{K}^+ \) and \( \text{SO}_4^{2-} \) 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.
We also determined the crystal axes by the back-reflection Laue method as shown in Figs. 23. We took Laue photographs in the arrangement shown in Fig. 23(a). The obtained Laue patterns are compared with the simulated Laue patterns as shown in Figs. 23(b) and (c). From the comparison, we found that the sample quality of the K-Fe-jarosite single crystal used in this study is very high, because the clear Laue pattern was observed, and all the reflection spots are undistorted and sharp.

Figure 23: (a) Experimental set-up for the Laue photograph measurement. (b) Laue photograph for the view from the c-axis. (c) Simulated Laue pattern for the view from the c-axis.
3.2.2 Magnetic susceptibility and specific heat

Figure 24 shows the temperature dependence of magnetic susceptibilities of single-crystalline KFe$_3$(OH)$_6$(SO$_4$)$_2$ at 3 T for $H || c$ and $H || ab$ ($H \perp c$) [34]. At high temperatures ($T > 150$ K), the susceptibility is isotropic and follows a Curie-Weiss law. Since the absolute value of the Weiss temperature exceeds largely the measured temperature range, the conventional Curie-Weiss law may not be applicable. Harris et al. calculated the uniform susceptibility $\chi$ of a kagome lattice using high-temperature expansions [16]. They showed that the $\chi$ deviates from the Curie-Weiss law due to the short-range correlation and is expressed at low temperatures as the corrected Curie-Weiss law $\chi = C'/(T + \Theta')$, where $C' = 8/9C$, $\Theta' = 3/2\Theta$, and $C$ and $\Theta$ are the conventional Curie constant and the Weiss temperature, respectively. Fits to this law between 150 K and 550 K yield the values $\Theta' = -800(30)$ K and $C' = 5.6(2)$ cm$^3$ K (mol$^{-1}$ Fe). The negative value $\Theta$ indicates that the nearest-neighbor interaction is antiferromagnetic. The Goodenough-Kanamori rule governing the frontier orbitals of the hydroxide-bridged iron trimer also predicts this antiferromagnetic exchange interaction. If the nearest-neighbor interaction in the kagome plane is dominant, the exchange constant $J$ is estimated to be about 40 K from $\Theta = -2zJS(S + 1)/3$ where $z = 4$ and $S = 5/2$. The effective Bohr magnetons $\mu_{\text{eff}}$ were evaluated to be 6.3(2) $\mu_B$, using $C = N\mu_{\text{eff}}^2/3k_B$ where $\mu_{\text{eff}} = g\mu_B\sqrt{S(S + 1)}$, and are in good accordance with the free-ion value 5.92$\mu_B$ for $g = 2$.

K-Fe-jarosite undergoes a three-dimensional (3D) long range order below the Neél temperature ($T_N$) 65 K. The ordering temperature $T_N$ is greatly reduced from the value $|\Theta|$ due to geometrical frustration. The frustration parameter $f = |\Theta|/T_N$ is about 12, indicating that this compound is highly frustrated. The inset shows $\chi(=M/H)$ measured for $H || c$ for designated magnetic fields of up to 14 T. The peak in the magnetic susceptibility for $H || c$ at $T = 65$ K indicates the presence of weak ferromagnetism along the $c$ direction. As mentioned above, a recent theoretical work shows that the DM interaction may induce such a magnetic moment by canting the spins slightly out of the plane. A single-ion-type anisotropy in the octahedron composed of six oxygens tilted from the principal axes [see Figs. 20(b), (c) and (d)] may become the origin of weak ferromagnetism. At low temperatures, the upturn in the susceptibilities at low temperatures can be described by a Curie tail $\chi = C/T$ due to paramagnetic impurities. It may be claimed that the upturn could arise from the DM interaction. The amplitudes of the upturns should be different for the field directions in the case of the DM origin, but we observed the similar upturns for both field directions in this figure. The concentration of impurities spins, when assuming $S = 5/2$, is evaluated to be ~0.3 % of the total spins.

Figure 25 shows the temperature dependence of the specific heat $C$ of powder samples of KFe$_3$(OH)$_6$(SO$_4$)$_2$ and KGa$_3$(OH)$_6$(SO$_4$)$_2$ [34]. The non-magnetic isostructural compound KGa$_3$(OH)$_6$(SO$_4$)$_2$ data are scaled to match the Fe jarosite data at high temperatures and are used to estimate the phonon contribution. A peak in the specific heat is found at the magnetic transition temperature of 65 K. The entropy associated with the 3D magnetic transition (integrating $C/T$ over the temperature range from 2 K to 100 K) represents ~50 % of the $Rln 6$ (where $R$ is the molar gas constant) total entropy expected for the spin-5/2 system. This suggests that short-range correlation has already formed at much higher temperatures.
Figure 24: Magnetic susceptibility versus temperature in the magnetic field at 3 T for two orientations, \( H \parallel c \) and \( H \parallel ab \). The inset shows magnetic susceptibilities for \( H \parallel c \) in the designated magnetic fields of up to 14 T [34].

Figure 25: Specific heat \( C \) data of powder samples of \( \text{KFe}_3(\text{OH})_6(\text{SO}_4)_2 \) (closed symbols) and the non-magnetic isostructural compound \( \text{KGa}_3(\text{OH})_6(\text{SO}_4)_2 \) (open symbols) as a function of temperature [34].
3.2.3 Magnetic structure

The elastic powder neutron scattering measurements were performed to determine the magnetic structure of KFe$_3$(OH)$_6$(SO$_4$)$_2$. Figure 26 shows the elastic powder neutron scattering data of deuterated KFe$_3$(OD)$_6$(SO$_4$)$_2$ obtained at (a) 100 K and (b) 7 K [36]. As already mentioned, extremely high degeneracy of the ground states prevents the long-range magnetic ordering at any temperature and the $\sqrt{3} \times \sqrt{3}$ spin structure is predicted theoretically to be favored rather than the $q = 0$ spin structure at $T=0$ in a simple kagome lattice Heisenberg antiferromagnet. Nevertheless, K-Fe-jarosite shows a long-range magnetic ordering at 65 K and the ordered magnetic structure was found to be the $q = 0$ spin structure. In addition, although the $q = 0$ spin structure has two degenerated states with “positive” and “negative” chirality, the observed magnetic structure contains only elemental triangles with positive chirality [see Fig. 26 (c)].

Nuclear magnetic resonance (NMR) measurements were performed to check the spin structure of KFe$_3$(OH)$_6$(SO$_4$)$_2$ [35]. Figure 27 shows the NMR spectra of K-Fe-jarosite obtained at (a) 71.2 K and (b) 1.76 K. The NMR spectra confirm the long-range magnetic ordering below 65 K and the same spin structure in the ordered phase. It is also expected some anisotropic term such as the DM interaction or the single ion anisotropy plays an important role in explaining this ordered spin structure.

The magnetic field ($H$) - temperature ($T$) phase diagram is shown in Fig. 58 [40]. A field-induced phase was observed at comparatively high magnetic fields above the transition field $H_c$ for $H||c$. This magnetic phase transition caused by a 180° rotation of all the spins on the layers that were oppositely canted against magnetic fields as shown in the inset of Fig. 58. However, there are few measurements above $H_c$ at low temperatures due to the requirement of a large magnetic field.
Figure 26: Elastic powder neutron scattering data of deuterated KFe$_3$(OD)$_6$(SO$_4$)$_2$ obtained at (a) 100 K and (b) 7 K. In each figure, observed (dotts), calculated (upper solid line) and their difference (lower solid line) of neutron-diffraction profiles of deuterated K jarosite. Vertical ticks indicate the positions of nuclear [(a) and upper row in (b)] and magnetic [lower row in (b)] Bragg reflections. Magnetic reflections are indexed in (b). (c) The best model of the magnetic structure for K jarosite. This structure is so-called $q = 0$ structure [36].
Figure 27: $^1$H-NMR spectra of KFe$_3$(OH)$_6$(SO$_4$)$_2$ at 75.1 MHz (a) above (71.2 K) and (b) below (1.76 K) the transition temperature. The broken line in (b) indicates the calculated powder pattern at proton sites. The $^{19}$F signal originates from the Teflon tape around the NMR coils [35].

Figure 28: K-Fe-jarosite phase diagram as a function of field and temperature. Blue circles show the results of the magnetization measurements. Open diamonds, green triangles, red triangles and red squares indicate the results of the neutron scattering measurements [40].
3.2.4 Inelastic neutron scattering measurements

The energy dispersion curves were obtained from inelastic neutron scattering measurements on a single-crystal sample as shown in Figs. 29(a) and (b). Matan et al. calculated the spin wave excitations in terms of two simple spin models [37]. In the first model, which is named the DM model, we neglect the single-ion anisotropy, so that nonzero parameters are $J$, $J_2$, $d_p$, and $d_z$ where $J$ and $J_2$ are the exchange constant between nearest-neighbor and next-nearest-neighbor spins in the kagome plane, respectively,

$$\mathcal{H} = J \sum_{<ij>} S_i \cdot S_j + J_2 \sum_{<ik>} S_i \cdot S_k + \sum_{<ij>} d_{ij} \cdot S_i \times S_j.$$  \hspace{1cm} (9)

In the second model, which is named the CF (crystal field) model, all the anisotropy is attributed to the single-ion crystal field anisotropy, so that nonzero parameters are $J$, $J_2$, $D$, and $E$ where $D$ and $E$ are the axial and the rhombic single ion anisotropy constants, respectively,

$$\mathcal{H} = J \sum_{<ij>} S_i \cdot S_j + J_2 \sum_{<ik>} S_i \cdot S_k + D \sum_i (S_i^\tau)^2 - E \sum_i \{(S_i^\tau)^2 - (S_i^\sigma)^2\}.$$  \hspace{1cm} (10)

In both cases, $J$ is the dominant interaction. The numerical results obtained from these two models are plotted with the solid lines in Fig. 29. In their analyses, good agreement between experiment and calculation was obtained by using the DM model [Fig. 29(a)]. Although there is no large difference between two analytical results, K. Matan et al. conclude the CF model [Fig. 29(b)] is unreasonable by the small splitting of spin wave mode at $\Gamma$ point. However, the origin of the anisotropy in K-Fe-jarosite is difficult to be determined from the neutron scattering experiments due to poor resolution.

![Energy dispersion curves](image)

Figure 29: Energy dispersion curves along the high symmetry directions in the 2D Brillouin zone at $T = 10$ K. As discussed in the text, the lines in (a) denote a fit to the DM model, with fitting parameters $J = 37$ K, $J_2 = 1.3$ K, $d_p = 2.2$ K, and $d_z = 2.2$ K. The lines in (b) denote a fit to the CF model, with fitting parameters $J = 39$ K, $J_2 = 1.4$ K, $D = 5.0$ K, and $E = 0.37$ K [37].
3.3 Experimental results

3.3.1 Magnetization

We performed magnetization measurements on a single crystal of K-Fe-jarosite for \( H \parallel c \) (\( H \parallel \text{kagome plane} \)) and \( H \parallel a \) (\( H \perp \text{kagome plane} \)).

\( H \parallel c \)

The magnetization curve at 4.2 K for \( H \parallel c \) is shown in Fig. 30. The curve with a broken line (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 of the subtracted data increases almost linearly with increasing field as shown with a solid line in Fig. 30. A steep increase, which corresponds to the magnetic transition reported previously [34, 40], 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 (inset of Fig. 26). The inset of Fig. 30 shows the field derivative of magnetization curve (\( dM/dH \)) observed at 4.2 K for \( H \parallel c \). A distinct peak around \( H_c=16.4 \) T, which we define as the critical field (\( H_c \)), is observed. Since there is a hysteresis near \( H_c \), this magnetic transition must be a first-order phase transition.

\( H \parallel a \)

Figure 31 shows the magnetization curve at 2 K for \( H \parallel a \). The magnetization curve drawn with a thick broken line (raw data) indicates a convex upward at low fields as well as the raw magnetization curve for \( H \parallel c \). In the same way, we subtract the paramagnetic contribution from the raw data. Then, the magnetization curve (subtracted data) increases almost linearly with increasing field as shown by the solid line in Fig. 29. No magnetic transition was observed in this magnetization curve up to 7 T.
Figure 30: Magnetization curve of a single crystal sample of K-Fe-jarosite at 4.2 K for $H\parallel c$ (field ascending process). Broken and solid lines are the raw magnetization curve and the magnetization subtracted the contribution of paramagnetic impurity from the raw data, respectively. The inset shows the field derivative of the magnetization at 4.2 K for $H\parallel c$.

Figure 31: Solid and broken lines represent the subtracted and raw magnetization curves of a single crystal sample of K-Fe-jarosite for $H\parallel a$, respectively.
3.3.2 Frequency dependence of ESR spectra

$H||c$

Figures 32 (a) and (b) show the frequency dependence of the ESR absorption spectra for $H||c$ 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 in Fig. 34. We detected ESR modes with zero-field gaps of about 1600 GHz and 350 GHz. The energy branches with the zero-field gaps were observed in the previous neutron scattering experiments [37]. We conclude that the observed ESR modes (closed circles) correspond to the excitation modes at $\Gamma$ point. The sharp signals corresponding to open circles in Fig. 34 must be electron paramagnetic resonance (EPR) signals from magnetic impurities.

$H||a$

In Fig. 33, it is shown the frequency dependence of the ESR absorption spectra for $H||a$ at 1.3 K in pulsed magnetic fields. We observed some broad resonance signals indicated by the closed circles and sharp signals indicated by the arrows. All the resonance fields are plotted in the frequency-field plane as shown in Fig. 35. We observed only one ESR branch with a zero-field gap of about 1600 GHz, while some ESR branches with the zero-field gaps of about 1600 GHz were observed for $H||c$. We conclude that this observed ESR branch corresponds to essentially the same branch observed for $H||c$. Sharp signals (open circles) also are considered to be paramagnetic resonance signals from magnetic impurities.
Figure 32: Frequency dependence of (a) ESR absorption spectra of K-Fe-jarosite for $H || c$ at 1.6 K in static magnetic fields and (b) those at 1.3 K in pulsed magnetic fields. The arrows, inverted triangles and circles indicate intrinsic ESR signals, paramagnetic signals from impurities and a baseline anomaly caused by the magnetic transition, respectively.

Figure 33: Frequency dependence of ESR absorption spectra of K-Fe-jarosite for $H || a$ at 1.3 K in pulsed magnetic fields. The closed circles and arrows indicate intrinsic ESR signals and paramagnetic signals from impurities, respectively.
Figure 34: Frequency-field diagram of K-Fe-jarosite for \( H/\parallel c \) at 1.3 K. Closed and open circles, and triangles denote the resonance fields of intrinsic signals, those of an impurity signal and an anomaly accompanied with the magnetic transition, respectively.

Figure 35: Frequency-field diagram of K-Fe-jarosite for \( H/\parallel a \) at 1.3 K. Closed and open circles denote the resonance fields of intrinsic signals and those of an impurity signal, respectively.
3.3.3 Temperature dependence of ESR spectra

Figures 36(a) and (b) show the temperature dependences of the ESR absorption spectra at 730.5 GHz for $H||c$ and $H||a$, respectively. As already mentioned, sharp signals come from magnetic impurities and thus are extrinsic. Immediately above $T_N$, we observed a very broad resonance signal for $H||c$, while some additional signal was observed at about 24 T both below and above $T_N$ for $H||a$. At highest temperature, we observed a broad signal around 26 T ($g=2.0$) for both cases. The reason for the splitting of the signal in the intermediate temperature region along the $a$-axis is unclear at present. ESR spectra having a large line width are probably caused by an inhomogeneous internal magnetic field produced with the development of short-range correlation. Such short-range correlation was also observed in specific heat as described in § 3.2.2. As shown in Figs. 35, the anisotropy of the $g$ values is quite small, and almost equivalent $g$ values are obtained for the $a$ axis ($g_a = 2.01 \pm 0.01$) and the $c$ axis ($g_c = 2.00 \pm 0.01$). Since FeO$_6$ octahedra incline as shown in Figs. 20(b) and (c), the principal $z$ axis is tilted from the $c$-axis about $\eta_{ef} = 20^\circ$. Then the angle dependence of $g$ value $g(\theta)$ is given by,

$$g(\theta) = \sqrt{g_{||}^2 \cos^2 (\theta - \eta_{ef}) + g_{\perp}^2 \sin^2 (\theta - \eta_{ef})},$$

(11)

where $g_{||}$ is the $g$ value parallel to the principal $z$-axis, and $g_{\perp}$ the $g$ value perpendicular to the $z$-axis, $\theta$ the angle between the $c$-axis and the external magnetic field [$g(0^\circ) = g_c, g(90^\circ) = g_a$]. The $g_{||}$ and $g_{\perp}$ values are obtained by this expression.
Figure 36: Temperature dependence of ESR spectra of a single crystal sample of K-Fe-jarosite at 730.5 GHz for (a) $H||c$ and (b) $H||a$.

Figure 37: EPR spectra of a single crystal sample of K-Fe-jarosite at 730.5 GHz for $H||c$ and $H||a$ at designated highest temperatures.
3.4 Analysis

3.4.1 Dzyaloshinsky-Moriya (DM) model

First, we analyze the frequency dependence of the ESR resonance fields and the magnetization curve, both for $H||c$. In this work, 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,

$$
\mathcal{H} = J \sum_{<ij>} S_i \cdot S_j + J_\perp \sum_{<lm>} S_i \cdot S_m + \sum_{<ij>} d_{ij} \cdot S_i \times S_j - g \mu_B \sum_i S_i \cdot H, \tag{12}
$$

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 the $i$-site, $J_\perp$ the inter-plane 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 $H = (0, 0, H)$ the external magnetic field. We ignore this NNN interaction $J_2$ for simplicity, since it is considered to be small enough.

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 [19]. In a perfect kagome lattice, the DM vectors can only be perpendicular to the kagome plane since this plane is a mirror plane in view of the symmetry. In the jarosites, the symmetry is lowered because the octahedra of oxygen atoms which surround the magnetic sites are tilted. The DM vectors exist in the mirror plane between the nearest $i$ and $j$ sites in the jarosite as shown in Fig. 38. Then, the DM interaction in jarosite is similar to one described in § 3.1.2. Here, we divide the DM vector into two components, $d_p$: the in-plane component and $d_z$: the $z$ component parallel to the $c$-axis for this analysis.

Elhajal et al. [20] and Yildirim et al. [54] discussed the DM interaction in a jarosite. The directions of the DM vectors seem to be 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. [40]. Elhajal et al. discussed theoretically the effects of $d_z$ 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 $d_z$ 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 $d_z$. Accordingly, $d_z > 0$ and $d_z < 0$ stabilize positive and negative chirality, respectively. In K-Fe-jarosite, the $q = 0$ structure with positive chirality was observed in powder neutron diffraction [36], thus $d_z > 0$ acting on this system. Elhajal et al. also discussed that all the spins have a weak $c$-axis component when $d_p$ is non-zero, 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. 12. 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° [40].

Figure 39 depicts the details of the exchange interactions in K-Fe jarosite. As shown in Fig. 40, 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,

$$F = A \sum_{ij} M_i \cdot M_j + B \sum_{lm} M_l \cdot M_m + \sum_{ij} d_{ij} M_i \times M_j - \sum_{i=1} M_i \cdot H. \quad (13)$$

Figure 38: Dzyaloshinsky-Moriya (DM) vector (thick green vector) and spin-canted state (red vectors) in K-Fe-jarosite. The DM vector exists in the mirror plane between $i$ and $j$ sites. The green thin vectors indicate projective components of the DM vector to kagome plane ($d_p$) and to the $c$-axis ($d_z$).

Figure 39: Exchange interactions in K-Fe jarosite. Dzyaloshinsky-Moriya (DM) vector (green vector) and canted spins (red and blue vectors) for $H < H_c$ and $H > H_c$. 

$$F = A \sum_{ij} M_i \cdot M_j + B \sum_{lm} M_l \cdot M_m + \sum_{ij} d_{ij} M_i \times M_j - \sum_{i=1} M_i \cdot H. \quad (13)$$
Figure 40: Details of magnetic structure and exchange interactions in K-Fe jarosite for (a) $H<H_c$ and (b) $H>H_c$.

Here, the coefficients and the vectors below $H_c$ are given by $A = 12J/(N(g\mu_B)^2)$, $B = 12J_1/(N(g\mu_B)^2)$, $\mathbf{d}_{ij} = 12\mathbf{d}_{ij}/(N(g\mu_B)^2)$, and $\mathbf{M}_i = N g \mu_B \mathbf{S}_i/6$. Above $H_c$, they are written as $A = 6J/(N(g\mu_B)^2)$, $B = 6J_1/(N(g\mu_B)^2)$, $\mathbf{d}_{ij} = 6\mathbf{d}_{ij}/(N(g\mu_B)^2)$, and $\mathbf{M}_i = N g \mu_B \mathbf{S}_i/3$. $N$ is the number of magnetic ions, and $\mathbf{M}_i$ is 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

$$\frac{\partial \mathbf{M}_i}{\partial t} = \gamma [\mathbf{M}_i \times \mathbf{H}_i],$$

where $\gamma$ is the gyromagnetic ratio and $\mathbf{H}_i$ a mean-field applied on the $i$-th sublattice moment given by

$$\mathbf{H}_i = -\frac{\partial F}{\partial \mathbf{M}_i}.$$  \hfill (15)

To solve the equation of motion, we use a method applied for $ABX_3$-type antiferromagnets [53]. 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,

$$\mathbf{M}'_i = ([|\mathbf{M}_i|, \Delta M_{iy} \exp(i\omega t), \Delta M_{iz} \exp(i\omega t)),$$

where $\Delta M_{iy}, \Delta M_{iz} \ll |\mathbf{M}_i|$, 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.
Fot $H < H_c$, eq. 13 can be expanded using six sublattice magnetic moments as,

$$F = -\sum_{i=1}^{6} M_i \cdot H + A (M_1 \cdot M_2 + M_2 \cdot M_3 + M_3 \cdot M_4 + M_4 \cdot M_5 + M_5 \cdot M_6 + M_6 \cdot M_1)$$

$$+ B (M_1 \cdot M_5 + M_1 \cdot M_6 + M_2 \cdot M_4 + M_2 \cdot M_6 + M_3 \cdot M_4 + M_3 \cdot M_5)$$

$$+ dt_{12} \cdot M_1 \times M_2 + dt_{23} \cdot M_2 \times M_3 + dt_{31} \cdot M_3 \times M_1$$

$$+ dt_{45} \cdot M_4 \times M_5 + dt_{56} \cdot M_5 \times M_6 + dt_{64} \cdot M_6 \times M_4.$$  \hspace{1cm} (17)

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. 41. Using angles shown in this figure, we express the sublattice magnetizations as

$$M_n = M_0 (\cos \theta_n \cos \eta_n, \sin \theta_n \cos \eta_n, \sin \eta_n),$$ \hspace{1cm} (18)

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

$$\theta_1 = 3\pi/2, \theta_2 = 5\pi/6, \theta_3 = \pi/6,$$

$$\theta_4 = \pi/2, \theta_5 = 11\pi/6, \theta_6 = 7\pi/6,$$

$$\eta_1 = \eta_2 = \eta_3, \eta_4 = \eta_5 = \eta_6.$$ \hspace{1cm} (19)

The DM components are given by,

$$dt_{12} = dt_{45} = (-\sqrt{3} dt_p/2, -dt_p/2, dt_z),$$

$$dt_{23} = dt_{56} = (0, dt_p, dt_z),$$

$$dt_{31} = dt_{64} = (\sqrt{3} dt_p/2, -dt_p/2, dt_z).$$ \hspace{1cm} (20)

Substituting eqs. 18, 19, and 20 into eq. 13, we have

Figure 41: Configuration of the sublattice magnetic moments for $H || c$ and $H < H_c$. 

49
\[
F = -H(3M_0 \sin \eta_1 + 3M_0 \sin \eta_4) \\
+ \frac{3}{4} AM_0^2 (2 - 3 \cos 2\eta_1 - 3 \cos 2\eta_4) \\
+ BM_0^2 (3 \cos \eta_1 \cos \eta_4 + 6 \sin \eta_1 \sin \eta_4) \\
- \frac{3}{2} \sqrt{3} dt z M_0^2 (\cos^2 \eta_1 + \cos^2 \eta_4) \\
+ \frac{3}{2} \sqrt{3} dt p M_0^2 (\sin 2\eta_1 - \sin 2\eta_4). 
\]

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

\[
M = 3M_0 (\sin \eta_1 + \sin \eta_4). 
\]

The transformation of new coordinates, \( \hat{x}, \hat{y} \) and \( \hat{z} \), system of the \( i \)-th sublattice can be performed by the matrix \( R_i \).

\[
R_i = \begin{pmatrix}
\cos \theta_i \cos \eta_i & \sin \theta_i \cos \eta_i & \sin \eta_i \\
-\sin \theta_i & \cos \theta_i & 0 \\
-\cos \theta_i \sin \eta_i & -\sin \theta_i \sin \eta_i & \cos \eta_i
\end{pmatrix}. 
\]

The transformed interaction matrix are such that

\[
M_i' = R_i M_i, \quad M_i = R_i^{-1} M_i'. 
\]

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,

\[
\frac{\partial M_i'}{\partial t} = \gamma R_i [(R_i^{-1} M_i') \times (R_i^{-1} H_i')], 
\]

where \( H_i' = R_i H_i \). Expressing eq. 25 with the matrix, we have

\[
\begin{pmatrix}
\frac{\partial M_{1v}'}{\partial t} \\
\frac{\partial M_{2v}'}{\partial t} \\
\frac{\partial M_{3v}'}{\partial t} \\
\frac{\partial M_{4v}'}{\partial t} \\
\frac{\partial M_{5v}'}{\partial t} \\
\frac{\partial M_{6v}'}{\partial t}
\end{pmatrix} = \frac{1}{\gamma} \tilde{M}, 
\]

\[
\tilde{M} = \begin{pmatrix}
M_{1v} \\
M_{2v} \\
M_{3v} \\
M_{4v} \\
M_{5v} \\
M_{6v}
\end{pmatrix}. 
\]

where

\[
\tilde{M} = \begin{pmatrix}
\tilde{M}_{vv} & \tilde{M}_{vy} \\
\tilde{M}_{vy} & \tilde{M}_{yy}
\end{pmatrix}. 
\]
Here,

\[
\tilde{M}_{yy} = \begin{pmatrix}
0 & -\alpha & 0 & 0 & \beta & -\beta \\
\alpha & 0 & -\alpha & -\beta & 0 & \beta \\
-\alpha & \alpha & 0 & \beta & -\beta & 0 \\
0 & \beta' & -\beta' & 0 & \alpha_2 & -\alpha_2 \\
-\beta' & 0 & \beta' & -\alpha_2 & 0 & \alpha_2 \\
\beta' & -\beta' & 0 & \alpha_2 & -\alpha_2 & 0
\end{pmatrix},
\]

(28)

\[
\alpha = \frac{M_0}{2} \left\{ dt_p \cos \eta_1 + (\sqrt{3}A - dt_z) \sin \eta_1 \right\},
\]

(29)

\[
\alpha_2 = \frac{M_0}{2} \left\{ dt_p \cos \eta_2 + (-\sqrt{3}A + dt_z) \sin \eta_2 \right\},
\]

(30)

\[
\beta = \frac{\sqrt{3}}{2} BM_0 \sin \eta_1,
\]

(31)

The \( \beta' \) in eq. 28 is given by the following replacement:

\[
\eta_1 \leftrightarrow \eta_4.
\]

(32)

\[
\tilde{M}_{yz} = \begin{pmatrix}
\gamma & \delta & \delta & 0 & \epsilon & \epsilon \\
\delta & \gamma & \delta & 0 & \epsilon & \epsilon \\
\delta & \delta & \gamma & 0 & \epsilon & \epsilon \\
0 & \epsilon & \epsilon & \gamma_2 & \delta_2 & \delta_2 \\
\epsilon & \epsilon & 0 & \delta_2 & \gamma_2 & \delta_2 \\
\epsilon & \epsilon & 0 & \delta_2 & \delta_2 & \gamma_2
\end{pmatrix},
\]

(33)

\[
\gamma = (A + \sqrt{3}dt_z) M_0 \cos^2 \eta_1
- \cos \eta_1 M_0 (B \cos \eta_4 + 2\sqrt{3} dt_p \sin \eta_1)
+ M_0 \sin \eta_1 (-2A \sin \eta_1 - 2B \sin \eta_4) + H \sin \eta_1
\]

(34)

\[
\gamma_2 = (A + \sqrt{3}dt_z) M_0 \cos^2 \eta_4
- \cos \eta_4 M_0 (B \cos \eta_4 - 2\sqrt{3} dt_p \sin \eta_4)
+ M_0 \sin \eta_4 (-2A \sin \eta_4 - 2B \sin \eta_1) + H \sin \eta_4
\]

(35)

\[
\delta = \frac{M_0}{4} (A - \sqrt{3}dt_z + (3A + \sqrt{3}dt_z) \cos 2\eta_1
- 2\sqrt{3}dt_p \sin 2\eta_1
\]

(36)

\[
\delta_2 = \frac{M_0}{4} (A - \sqrt{3}dt_z + (3A + \sqrt{3}dt_z) \cos 2\eta_4
+ 2\sqrt{3}dt_p \sin 2\eta_4
\]

(37)

\[
\epsilon = \frac{BM_0}{2} (2 \cos \eta_1 \cos \eta_4 + \sin \eta_1 \sin \eta_4),
\]

(38)
\[ \tilde{M}_{xy} = \begin{pmatrix} -\gamma & \sigma & \sigma & 0 & \tau & \tau \\ \sigma & -\gamma & \sigma & \tau & 0 & \tau \\ \sigma & \sigma & -\gamma & \tau & \tau & 0 \\ 0 & \tau & \tau & -\gamma_2 & \sigma & \sigma \\ \tau & 0 & \tau & \sigma & -\gamma_2 & \sigma \\ \tau & \tau & 0 & \sigma & \sigma & -\gamma_2 \end{pmatrix}, \]  
(39)

\[ \sigma = \frac{M_0}{2} (A + \sqrt{3} dt_x), \]  
(40)

\[ \tau = -\frac{BM_0}{2}, \]  
(41)

\[ \tilde{M}_{zz} = \begin{pmatrix} 0 & -\alpha & \alpha & 0 & \beta' & -\beta' \\ -\alpha & 0 & -\alpha & -\beta' & 0 & \beta' \\ -\alpha & -\alpha & 0 & \beta' & -\beta' & 0 \\ 0 & \beta & -\beta & 0 & \alpha_2 & -\alpha_2 \\ -\beta & 0 & \beta & -\alpha_2 & 0 & \alpha_2 \\ \beta & -\beta & 0 & \alpha_2 & -\alpha_2 & 0 \end{pmatrix}. \]  
(42)

Substituting eq. 25 into eq. 26, we have

\[ (\tilde{M} - i\omega/\gamma E) \begin{pmatrix} \Delta M_{1y} \\ \Delta M_{2y} \\ \Delta M_{3y} \\ \Delta M_{4y} \\ \Delta M_{5y} \\ \Delta M_{6y} \\ \Delta M_{1z} \\ \Delta M_{2z} \\ \Delta M_{3z} \\ \Delta M_{4z} \\ \Delta M_{5z} \\ \Delta M_{6z} \end{pmatrix} = 0, \]  
(43)

where E is a unit matrix. Theoretical ESR resonance modes for \( H < H_c \) correspond to the absolute eigenvalues of \( \omega/\gamma \). We obtain the eigenvalues by solving this secular equation.

For \( H > H_c \) case, the angles \( \theta_n \) and \( \eta_n \) are given by

\[ \theta_1 = \pi/2, \theta_2 = 11\pi/6, \theta_3 = 7\pi/6, \]
\[ \eta_1 = \eta_2 = \eta_3. \]  
(44)

The following calculation process is essentially similar to that for \( H < H_c \). Substituting eqs. 18, 20, and 44 into eq. 13, we have

\[ F = -3HM_0 \sin \eta_1 + \frac{3}{4} AM_0^2 (1 - 3 \cos 2\eta_1) - \frac{3}{2} \sqrt{3} dt_x M_0^2 \cos^2 \eta_1 - \frac{3}{2} \sqrt{3} dt_x M_0^2 \sin 2\eta_1 + \frac{3}{4} BM_0^2 (1 - 3 \cos 2\eta_1). \]  
(45)
The angles $\eta_1$ is determined by $\partial F/\partial \eta_1 = 0$ numerically. The magnetization $M$ induced along the $c$-axis is expressed

$$M = 3M_0 \sin \eta_1,$$

(46)

where $M_0 = (N/3)\mu_B|S|$. Theoretical ESR resonance modes of the DM model for $H > H_c$ correspond to the absolute eigenvalues for the following matrix,

$$\tilde{M}_{\text{above}} = \begin{pmatrix}
0 & -\alpha_{ab} & \gamma_{ab} & \beta_{ab} & \beta_{ab} \\
-\alpha_{ab} & 0 & -\alpha_{ab} & \beta_{ab} & \gamma_{ab} \\
\epsilon_{ab} & \chi_{ab} & \chi_{ab} & 0 & -\alpha_{ab}
\end{pmatrix},$$

(47)

where

$$\alpha_{ab} = \frac{M_0}{2} \left\{ -d_{tp} \cos \eta_1 + (\sqrt{3}A + \sqrt{3}B - dt_z) \sin \eta_1 \right\},$$

(48)

$$\beta_{ab} = \frac{M_0}{4} \left\{ A + B - \sqrt{3}dt_z + (3A + 3B + \sqrt{3}dt_z) \cos 2\eta_1 \\
+ 2\sqrt{3}d_{tp} \sin 2\eta_1 \right\},$$

(49)

$$\gamma_{ab} = M_0 \left\{ (A + B + \sqrt{3}dt_z) \cos^2 \eta_1 + \sqrt{3}d_{tp} \sin 2\eta_1 \\
- 2(A + B) \sin^2 \eta_1 \right\} + H \sin \eta_1,$$

(50)

$$\beta_{ab} = \frac{M_0}{2} \left\{ A + B - \sqrt{3}dt_z - (3A + 3B + \sqrt{3}dt_z) \cos 2\eta_1 \\
- 2\sqrt{3}d_{tp} \sin 2\eta_1 \right\} - H \sin \eta_1,$$

$$\chi_{ab} = \frac{M_0}{2} \{ A + B + \sqrt{3}dt_z \}$$

(51)

We obtain the eigenvalues for $H > H_c$ by solving this secular equation as well.

As shown in Figs. 42, we get good agreement between experiment and calculation using the following parameters, $J/k_B = 42.3$ K, $J_{\perp}/k_B = -9.66 \times 10^{-2}$ K, $d_p/k_B = 1.62$ K, $d_z/k_B = 1.97$ K, and $g_c = 2.00$. The details of determination of these parameters will be described in the next discussion section. The $g$-values $g_c$ is determined by ESR signal at 294 K (paramagnetic phase). The canting angle $\eta$ at 0 T is evaluated to be $1.23^\circ$.

Next, we analyze the frequency dependence of the ESR resonance fields and the magnetization curve for $H \parallel \mathbf{a}$, $\mathbf{H} = (H, 0, 0)$ in similar manners to above calculations. As shown in Figs. 43, we obtained good agreement between experiment and calculation using the same parameters except the $g$-value.
Figure 42: Comparison of the magnetization curve and the ESR modes of K-Fe-jarosite for $H \parallel c$ between experiment and calculation for the DM model. (a) Solid and broken lines represent the experimental (4.2 K) and calculated (0 K) magnetization curves, respectively. The subtracted data in Fig. 28 is used as the experimental result. (b) Frequency-field plot of the experimental and calculated resonance fields for $H \parallel c$. The experimental data are the same as those in Fig. 32. The solid lines show the calculated ESR modes and the thin broken line represents a paramagnetic-resonance line with $g=2.0$. 
Figure 43: Comparison of the magnetization curve and the ESR modes of K-Fe-jarosite for $H//a$ between experiment and calculation for the DM model. (a) Solid and broken lines represent the experimental (4.2 K) and calculated (0 K) magnetization curves, respectively. The subtracted data in Fig. 29 is used as the experimental result. (b) Frequency-field plot of the experimental and calculated resonance fields for $H//a$. The experimental data are the same as those in Fig. 33. The solid lines show the calculated ESR modes and the thin broken line represents a paramagnetic-resonance line.
3.4.2 Crystal field (CF) model

We analyze the experimental data by the following spin Hamiltonian assuming single-ion anisotropies (D and E). We call this model crystal field (CF) model, and the spin Hamiltonian of this model is written as,

\[
\mathcal{H} = J \sum_{<ij>} S_i \cdot S_j + J_\perp \sum_{<lm>} S_i \cdot S_m + D \sum_i (S_i^z)^2 - E \sum_i \{(S_i^x)^2 - (S_i^y)^2 \} - g\mu_B \sum_i S_i \cdot H
\]

where the \(z', y'\)-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. 44. The \(z'\)-axis is tilted from the \(c\)-axis about \(20^\circ\). The single-ion anisotropies were discussed in a previous paper on powder neutron scattering experiment \[36\]. 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 \(FeO_6\) octahedron along the \(z'\)-axis is larger than that in the \(x'y'\)-plane. In this manner, the single ion anisotropies may generate spin arrangement in the present study. The free energy \(F\) is expressed by the following form using a mean-field approximation,

\[
F = A \sum_{<ij>} M_i \cdot M_j + B \sum_{<lm>} M_i \cdot M_m + K \sum_i (M_{CFi}^z)^2 - C \sum_i \{(M_{CFi}^x)^2 - (M_{CFi}^y)^2 \} - \sum_i M_i \cdot H
\]

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 \(H_c\).

In the case of CF model, we have to consider the new coordinate, \(x', y', z'\).

\[
(M_{CFi}^x, M_{CFi}^y, M_{CFi}^z) = R_{CFi} M_i, \quad (54)
\]

where

\[
R_{CFi} = \begin{pmatrix}
\cos \theta_{cf1} \cos \eta_{cf} & \sin \theta_{cf1} \cos \eta_{cf} & \sin \eta_{cf} \\
-\sin \theta_{cf1} \cos \eta_{cf} & \cos \theta_{cf1} & 0 \\
-\cos \theta_{cf1} \sin \eta_{cf} & -\sin \theta_{cf1} \sin \eta_{cf} & \cos \eta_{cf}
\end{pmatrix}, \quad (55)
\]

\[
\theta_{cf1} = \theta_{cf4} = 3\pi/2, \\
\theta_{cf2} = \theta_{cf5} = 5\pi/6, \\
\theta_{cf3} = \theta_{cf6} = \pi/6, \\
\eta_{cf} = -20\pi/180 = -\pi/9.
\]

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Figure 44: Local environment and coordination around Fe$^{3+}$. The local principal $z'$-axis is parallel to the O(2)-Fe-O(2) 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.

Substituting eqs. 18, 19, 54, 55, and 56 into eq. 53, we have

$$F = -H(3M_0 \sin \eta_1 + 3M_0 \sin \eta_4)$$

$$+ \frac{3}{4} AM_0^2 (2 - 3 \sin 2 \eta_1 - 3 \sin 2 \eta_4)$$

$$+ BM_0^2 (3 \cos \eta_1 \cos \eta_4 + 6 \sin \eta_1 \sin \eta_4)$$

$$+ 3KM_0^2 (\sin^2 (\eta_1 - \eta_{cf}) + \sin^2 (\eta_4 + \eta_{ef}))$$

$$- 3CM_0^2 (\cos^2 (\eta_1 - \eta_{cf}) - \cos^2 (\eta_4 + \eta_{ef})), \quad (57)$$

The following calculation process is essentially similar to the DM model. Theoretical ESR resonance modes for the CF model correspond to the absolute eigen values for the following matrix,

$$\tilde{M}_{CF} = \begin{pmatrix} \tilde{M}_{yyCF} & \tilde{M}_{yzCF} \\ \tilde{M}_{zyCF} & \tilde{M}_{zzCF} \end{pmatrix}. \quad (58)$$

where

$$\tilde{M}_{yyCF} = \begin{pmatrix} 0 & -\alpha_{ef} & \alpha_{cf} & 0 & \beta_{cf} & -\beta_{ef} \\ -\alpha_{ef} & 0 & -\alpha_{ef} & -\beta_{ef} & 0 & \beta_{ef} \\ \alpha_{cf} & -\alpha_{ef} & 0 & \beta_{cf} & -\beta_{ef} & 0 \\ 0 & \beta_{cf} & -\beta_{ef} & 0 & -\alpha_{ef} & \alpha_{cf} \\ -\beta_{cf} & \beta_{ef} & -\alpha_{cf} & 0 & -\alpha_{ef} & \alpha_{cf} \\ \beta_{ef} & -\beta_{cf} & -\alpha_{cf} & -\alpha_{ef} & 0 & 0 \end{pmatrix}. \quad (59)$$

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\[ \alpha_{ef} = \frac{\sqrt{3}}{2} A M_0 \sin \eta_1, \quad (60) \]
\[ \beta_{ef} = \frac{\sqrt{3}}{2} B M_0 \sin \eta_1, \quad (61) \]
\[ \tilde{M}_{yz\,CF} = \begin{pmatrix} \gamma_{ef} & \delta_{ef} & \delta_{ef} & 0 & \epsilon_{ef} & \epsilon_{ef} \\ \delta_{ef} & \gamma_{ef} & \delta_{ef} & \epsilon_{ef} & 0 & \epsilon_{ef} \\ \delta_{ef} & \delta_{ef} & \gamma_{ef} & \epsilon_{ef} & \epsilon_{ef} & 0 \\ 0 & \epsilon_{ef} & \epsilon_{ef} & \gamma_{ef2} & \delta_{ef} & \delta_{ef} \\ \epsilon_{ef} & 0 & \epsilon_{ef} & \delta_{ef} & \gamma_{ef2} & \delta_{ef} \\ \epsilon_{ef} & \epsilon_{ef} & 0 & \delta_{ef} & \delta_{ef} & \gamma_{ef2} \end{pmatrix}, \quad (62) \]
\[ \gamma_{ef} = -\frac{A}{2} M_0 + \frac{3A}{2} M_0 \cos 2\eta_1 \]
\[ + 2(K - C) M_0 \cos 2(\eta_{cf} - \eta_1) \]
\[ - B M_0 \cos \eta_1 \cos \eta_4 - 2 B M_0 \sin \eta_1 \sin \eta_4 + H \sin \eta_1, \quad (63) \]
\[ \gamma_{ef2} = -\frac{A}{2} M_0 + \frac{3A}{2} M_0 \cos 2\eta_4 \]
\[ + 2(K - C) M_0 \cos 2(\eta_{ef} + \eta_4) \]
\[ - B M_0 \cos \eta_1 \cos \eta_4 - 2 B M_0 \sin \eta_1 \sin \eta_4 + H \sin \eta_4, \quad (64) \]
\[ \delta_{ef} = \frac{AM_0}{4} (1 + 3 \sin 2\eta_1), \quad (65) \]
\[ \epsilon_{ef} = B M_0 (\cos \eta_1 \cos \eta_4 + \frac{1}{2} \sin \eta_1 \sin \eta_4), \quad (66) \]
\[ \tilde{M}_{zy\,CF} = \begin{pmatrix} \rho_{ef} & \sigma_{ef} & \sigma_{ef} & 0 & \tau_{ef} & \tau_{ef} \\ \sigma_{ef} & \rho_{ef} & \sigma_{ef} & \tau_{ef} & 0 & \tau_{ef} \\ \sigma_{ef} & \sigma_{ef} & \rho_{ef} & \tau_{ef} & \tau_{ef} & 0 \\ 0 & \tau_{ef} & \tau_{ef} & \rho_{ef2} & \sigma_{ef} & \sigma_{ef} \\ \tau_{ef} & 0 & \tau_{ef} & \sigma_{ef} & \rho_{ef2} & \sigma_{ef} \\ \tau_{ef} & \tau_{ef} & 0 & \sigma_{ef} & \sigma_{ef} & \rho_{ef2} \end{pmatrix}, \quad (67) \]
\[ \rho_{ef} = M_0 \left\{ \frac{1}{2} A + 3 C + K - \frac{3}{2} A \cos 2\eta_1 \right\} \]
\[ + (C - K) \cos 2(\eta_{ef} - \eta_1) \]
\[ + B \cos \eta_1 \cos \eta_4 + 2 B \sin \eta_1 \sin \eta_4 \right\} - H \sin \eta_1, \quad (68) \]
\[ \rho_{ef2} = M_0 \left\{ \frac{1}{2} A + 3 C + K - \frac{3}{2} A \cos 2\eta_4 \right\} \]
\[ + (C - K) \cos 2(\eta_{ef} + \eta_4) \]
\[ + B \cos \eta_1 \cos \eta_4 + 2 B \sin \eta_1 \sin \eta_4 \right\} - H \sin \eta_4, \quad (69) \]
\[ \sigma_{ef} = \frac{AM_0}{2} \quad (70) \]
\[ \tau_{ef} = \frac{BM_0}{2} \quad (71) \]
The matrix elements with prime are given by the same replacement indicated in the replacement eq. 32. We obtain the eigenvalues for \( H < H_c \) by solving this secular equation in the same way.

In the case of \( H > H_c \), the following calculation process is essentially similar to that for \( H > H_c \) of the DM model. The free energy \( F \) can be written as

\[
F = -3HM_0 \sin \eta_1 + \frac{3}{4}AM_0^2 (1 - 3 \cos 2\eta_1) + \frac{3}{4}BM_0^2 (1 - 3 \cos 2\eta_1) + 3K M_0^2 \sin^2(\eta_{cf} + \eta_1) - 3C M_0^2 \cos^2(\eta_{cf} + \eta_1).
\]  

Theoretical ESR resonance modes for \( H > H_c \) of the CF model correspond to the absolute eigenvalues for the following matrix and are obtained by solving the secular equation.

\[
\tilde{M}_{CFAbove} =
\begin{pmatrix}
0 & -\alpha_{cfab} & \alpha_{cfab} & \gamma_{cfab} & \beta_{cfab} & \beta_{cfab} \\
-\alpha_{cfab} & 0 & -\alpha_{cfab} & \beta_{cfab} & \gamma_{cfab} & \beta_{cfab} \\
\epsilon_{cfab} & \chi_{cfab} & \chi_{cfab} & 0 & -\alpha_{cfab} & \alpha_{cfab} \\
\chi_{cfab} & \epsilon_{cfab} & \chi_{cfab} & \alpha_{cfab} & 0 & -\alpha_{cfab} \\
\chi_{cfab} & \chi_{cfab} & \epsilon_{cfab} & -\alpha_{cfab} & \alpha_{cfab} & 0
\end{pmatrix},
\]  

\[
\alpha_{cfab} = \frac{\sqrt{3}M_0}{2}(A + B) \sin \eta_1,
\]

\[
\beta_{cfab} = \frac{M_0}{4}(A + B)(1 + 3 \cos 2\eta_1),
\]

\[
\gamma_{cfab} = \frac{M_0}{2}[(A + B)(-1 + 3 \cos 2\eta_1) + 4(K - C) \cos(2(\eta_1 + \eta_{cf}))] + H \sin \eta_1,
\]

\[
\epsilon_{cfab} = \frac{M_0}{2}[(A + B)(1 - 3 \cos 2\eta_1) + 6C + 2K + 2(C - K) \cos(2(\eta_1 + \eta_{cf}))] + H \sin \eta_1,
\]

\[
\chi_{cfab} = \frac{M_0}{2}(A + B).
\]
The magnetization is calculated in the same way as in the previous subsection. We also analyze the frequency dependence of the ESR resonance fields and the magnetization curve for $H \parallel a \ [H = (H, 0, 0)]$.

As shown in Figs. 45(a) and 46(a), we have good agreement between experiment and calculation (#1) for both magnetization curves using the following parameters, $J/k_B = 42.3$ K, $J_\perp/k_B = -9.66 \times 10^{-2}$ K, $D/k_B = 8.29$ K, $E/k_B = 0.522$ K and the same $g$ values as in the analyses of the DM model. The canting angle at 0 T is evaluated to be $1.21\degree$. However, poor agreement is attained between experiment and calculation for the ESR modes, especially the high frequency ones [see Figs. 45(b) and 46(b)]. We 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. 45 and 45. For this fitting, we use the following parameters: $J/k_B = 42.3$ K, $J_\perp/k_B = -5.51 \times 10^{-2}$ K, $D/k_B = 4.64$ K, $E/k_B = 0.322$ K, and the same $g$ values as in the analyses of the DM model. The canting angle at 0 T is evaluated to be $0.70\degree$. 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 cannot be reproduced by the same parameters.
Figure 45: Comparison of the magnetization curve and the ESR modes of K-Fe-jarosite between experiment and calculation for the CF model. (a) Solid and two kinds of broken lines are experimental (4.2 K) and calculated (0 K) magnetization curves, respectively. The difference between calculations #1 and #2 are described in the text. (b) Frequency-field plot of the resonance fields for $H||c$. The symbols are identical to those in Fig. 32. The solid and broken lines indicate the calculated ESR modes using two different sets of parameters (calculations #1 and #2) and the thin dotted line represents a paramagnetic-resonance line with $g=2$. 
Figure 46: Comparison of the magnetization curve and the ESR modes of K-Fe-jarosite between the experiment and the calculation for the CF model. (a) Solid, broken dotted lines represent the experimental (2 K) and two kinds of calculated (0 K) magnetization curves, respectively. The subtracted data in Fig. 29 is used as the experimental result. (b) Frequency-field plot of the resonance fields for $H//a$. The symbols are identical to those in Fig. 33. The solid and broken lines indicate the calculated ESR modes using two different sets of parameters (calculations #1 and #2) and the thin broken line represents a paramagnetic-resonance line with $g=2$. 

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3.5 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 Fig. 40(a)), because the slope is proportional to $1/J$. We assume that the magnetic structure changes at $H_c$ with an umbrella structure upon increasing magnetic field as illustrated in Fig. 37. The magnetic transition observed at 16.4 T is interpreted as a flop of the weak ferromagnetic component. The relational expression [20] between the canting angle $2\eta$ and the intra-plane exchange and DM parameters is given by $\tan 2\eta = 2d_p/((\sqrt{3}J + d_z)$.

When $J \gg d_z$, 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 energy dispersion, is described by $S\sqrt{12}|d_p|$ [37]. 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 $d_z$ from zero field gap of the higher ESR mode. Then, we extract the value of $J_1$ from the comparison of the free energies calculated for $H<H_c$ and $H>H_c$. In this analysis, we expect the energy crossing occurs at 16.4 T, where the $dM/dH$ shows a distinct peak. This field-induced transition is explained by a competition between the interlayer coupling $J_1$ and the Zeeman energy. The following relation is given in [34]: $H_cS \sin \eta = 2S^2|J_1|$. Since $\sin \eta$ is very small, $H_c$ becomes large in spite of small $J_1$.

In the analyses of the CF model, we evaluate the $J$ and $J_\perp$ values in the same manner as in the analyses for the DM model. We also determine the values of single ion anisotropy constants $D$ and $E$ from the magnetization jump and the zero field gap of the ESR modes. But the magnetization jump and the high ESR modes are not simultaneously reproduced as we described in § 3.4.2. The $D$ value evaluated in this analysis is also too large in typical inorganic materials with Fe$^{3+}$ ions. It is generally accepted that the $D$ and $E$ values are small for Fe$^{3+}$ ($L=0$) except for a special ligand field environment such as met-myglobin [55]. In addition, we performed the calculations including higher order spin Hamiltonian term, $\alpha(S_x^A + S_y^A + S_z^A)$. 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 2, 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 $|d|\sim (\Delta g/g)J$ [19] where $\Delta g$ is the difference of $g$ values in the systems. As shown in Fig. 35, 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 ($\Delta g = g\parallel - g\perp$), 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.
Table 2: The comparison of the DM components in kagome-lattice samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_z$ (K)</th>
<th>$d_p$ (K)</th>
<th>$d$ (K)</th>
<th>$(\Delta g/g)J$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Fe-jarosite (present study)</td>
<td>1.62</td>
<td>1.97</td>
<td>2.55</td>
<td>0.275</td>
</tr>
<tr>
<td>K-Fe-jarosite [37]</td>
<td>2.27</td>
<td>2.29</td>
<td>3.22</td>
<td>-</td>
</tr>
<tr>
<td>Ag-Fe-jarosite [40]</td>
<td>1.97</td>
<td>2.09</td>
<td>2.87</td>
<td>-</td>
</tr>
<tr>
<td>Herbertsmithite [56]</td>
<td>15</td>
<td>2</td>
<td>15.1</td>
<td>30.2</td>
</tr>
<tr>
<td>Cs$_2$Cu$_3$HfF [31]</td>
<td>-</td>
<td>4.52</td>
<td>-</td>
<td>70.9</td>
</tr>
<tr>
<td>Cs$_2$Cu$_3$ZrF [31]</td>
<td>-</td>
<td>6.10</td>
<td>-</td>
<td>61.6</td>
</tr>
</tbody>
</table>

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$^\circ$ 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) [50, 44], hexagonal tungsten bronze (HTB)-type FeF$_3$ (Fe:S=5/2) [57], and A$_2$Cu$_3$BF$_{12}$ type materials (Cs$_2$Cu$_3$ZrF$_{12}$, Cs$_2$Cu$_3$SnF$_{12}$, and Cs$_2$Cu$_3$HfF$_{12}$ (Cu:S=1/2) [31]). Neutron scattering studies on (HTB)-type FeF$_3$ clarified the $q = 0$ structure below $T_N$ [57]. In addition, previous studies on Cr-jarosite and some A$_2$Cu$_3$BF$_{12}$ indicated the presence of weak ferromagnetism [31, 44]. The observed $q = 0$ structure and weak ferromagnetism in K-Fe-jarosite must be ascribed to positive $d_z$ and $d_p$, 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), volbosite (Cu:S=1/2), vesignieite (Cu:S=1/2), and Rb$_2$Cu$_3$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”. If the spin and the DM interaction are small enough, it might be possible to realize some sort of “spin liquid state”. The ground state of the $S$=1/2 kagome-lattice antiferromagnet has been discussed, and theoretical studies suggest the possibility of new phases including a spin liquid 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 $d_z \sim 0.1J$ [58]. Accordingly, it is expected that the ground state of a Heisenberg kagome-lattice antiferromagnet is altered drastically by the DM interaction, the value of spin and a change of exchange interactions caused by a lattice distortion.
3.6 Conclusions

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 $T=1.3$ K and 1.6 K, and a stepwise magnetization at 4.2 K for $H\parallel c$ and $a$. We conclude that the DM interaction is most dominant perturbation term which 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: $J/k_B= 42.3$ K, $d_p/k_B= 1.62$ K, $d_z/k_B =1.97$ K, $J_1/k_B= -9.66 \times 10^{-2}$ K, and $g_c = 2.00$. The magnetic transition at 16.4 T is caused by the change of spin structure which arises from the competition between the DM and the interplanar interaction.
4 S=5/2 triangular lattice antiferromagnet

\( \text{CuFe}_{1-x}\text{Ga}_x\text{O}_2 \)

4.1 Introduction

4.1.1 Classical triangular lattice antiferromagnet

A triangular lattice antiferromagnet has the simplest frustrated structure, and lots of compounds have been synthesized so far. Thus, triangular lattice antiferromagnets have been studied extensively both theoretically and experimentally. In a classical triangular lattice antiferromagnet, the ground state properties change with the anisotropy of the spin.

Classical Ising triangular lattice antiferromagnet

First, we mention an Ising spin system in which the strongest frustration is expected between classical spins. Wannir showed strictly that a long range order does not exist at finite temperature. This system was also found to have the ground state entropy of 0.323\( R \) as compared to the full spin entropy of 0.693\( R \) \[1\]. Namely, \( 2^{0.323/0.693}N \) macroscopic numbers of spin states degenerate in the ground state. Thus, the Ising spin cannot avoid spin frustration since there is no rotation flexibility of the spin.

Classical XY triangular lattice antiferromagnet

The ground state of classical XY triangular lattice antiferromagnet has a 120° spin structure. Since there is inplane rotational flexibility of spins in the XY spin system, the spin system releases frustration partially by realizing a noncollinear 120° spin structure. As shown in Fig. 47, chirality shows a staggered order with the positive and negative sign when spins are arranged in a 120° spin structure. Although the spin ordering at finite temperatures does not take place due to the Mermin-Wagner theorem \[59\], interesting behavior is expected at low temperatures. Miyashita and Shiba showed that the "chiral order" and Kosterlitz-Thouless (KT) transition occurs in the XY triangular lattice antiferromagnet by means of Monte Carlo simulations at \( T_{ch} = 0.513J \) and \( T_{KT} = 0.502J \), respectively \[11\]. Since the system does not show any long-range magnetic order, all of these transitions are the phase transitions without symmetry breaking.

Classical Heisenberg triangular lattice antiferromagnet

The ground state of classical Heisenberg triangular lattice antiferromagnet also has a 120° spin structure. However, in the case of Heisenberg spin system, since the rotational plane of 120° spin structure is not fixed, chirality vectors can also turn to arbitrary directions. Basically, the classical Heisenberg triangular lattice antiferromagnet does not show any "chiral order", since the chirality vectors have continuous three-dimensional rotational flexibility. Kawamura and Miyashita, however, demonstrated that the Heisenberg triangular lattice antiferromagnet bears a topologically stable point defect characterized by a two-valued topological quantum number, a Z\(_2\) vortex, at low temperatures by a Monte Carlo simulation \[60\]. The Z\(_2\) vortex is regarded as a vortex formed by chirality vectors. A snapshot of the Z\(_2\) vortex observed in the Monte Carlo simulation is shown in Fig. 48 (a), and a corresponding snapshot
of the equilibrium spin configuration is shown in Fig. 48 (b) [60].

Figure 47: Staggered spin chirality configuration appeared in a 120° spin structure of the XY triangular lattice antiferromagnet

Figure 48: A typical snapshot of the $Z_2$ vortex configuration observed in the Monte Carlo simulation reported in Ref. 60. (a) Arrows with open triangles denote chirality vectors in upward directions whereas arrows with solid triangles denote chirality vectors in downward directions. The radius of a circle represents the length of each chirality vector and the hexagram symbol denotes the vortex position. (b) Arrows denote the corresponding spin configurations [60].
4.1.2 Spin-lattice coupling in triangular lattice antiferromagnet

Frustrated magnets, in which classical ground states have multiple accidental degeneracies, have been at the focus of renewed attention. While much theoretical work has focused on the lifting of this degeneracy by thermal or quantum fluctuations, different mechanisms might dominate in real materials. As already mentioned in 1. 2, one mechanism of lifting of the degeneracy in frustrated magnets is the coupling of magnetism to the lattice (spin-lattice coupling). Indeed, the interaction between spin, lattice, and orbital degrees of freedom is central to understanding correlated materials [61]. In quantum spin system (small spins), previous studies have highlighted the role of lattice distortions in promoting valence bond physics (spin Pierels effect). In classical spin system (the opposite limit of quantum spins), the lattice coupling induced the stabilization of collinear ground states. Here, we will mention the effect of spin-lattice interactions on the ground states of the triangular lattice in the classical limit.

Wang and Vishwanath discussed the spin-lattice coupling in a classical triangular lattice antiferromagnet [62]. Spin-lattice couplings arise from the bond length dependence of the exchange interaction $J(r)$ as shown in Fig. 49(a). They use the following spin Hamiltonian,

$$\mathcal{H} = J \sum_{\langle ij \rangle} (1 - \alpha \frac{u_{ij}}{d}) S_i \cdot S_j + \frac{K}{2} \sum_{\langle ij \rangle} u_{ij}^2,$$

(80)

where $u_i$ is the displacement of site $i$ and hence $u_{ij} = (u_i - u_j) \cdot e_{ij}$ is the change in length of the bond $ij$ ($e_{ij}$ is the unit vector from site $i$ to $j$), the lattice constant is $d$ and $\alpha = dJ^{-1} \partial J/\partial r$. Using $\partial \mathcal{H}/\partial u_{ij} = 0$ we have (integrating out the phonons generates),

$$\mathcal{H} = J \left[ \sum_{\langle ij \rangle} S_i \cdot S_j - c(S_i \cdot S_j)^2 \right],$$

(81)

where $c$ is expressed $\alpha^2 J S^2/(2K)$.

While the regular $120^\circ$ spin structure well known for the Heisenberg triangular antiferromagnet is realized at $c = 0$, this is expected to survive to finite $c$ as well. On increasing the spin-phonon coupling $c$, the $120^\circ$ spin structure is followed first by the 4 sublattice (4SL) state, then an 8 sublattice state and finally the stripe S state as shown in Fig. 49(b). Apparently, collinear states are preferred for large $c$. As shown in Fig. 49(c), the phase diagram in a magnetic field is remarkably complex, with magnetization plateaus at $f=1/5$th, 1/3rd, 3/7th, 3/5th, 5/7th, and 1/2nd of the total magnetization. These suggest that spin-lattice couplings may play important role in real materials.
Figure 49: (a) Picture of the spin-lattice coupling between site $i$ and $j$. All the notations are described in the text. (b) Zero-field phase diagram of the triangular lattice antiferromagnet with spin-lattice coupling as a function of $c$. Solid blue (open red) circles represent up (down) spins. (c) $T = 0$ phase diagram of the triangular lattice spin-lattice coupling model. Dashed lines are continuous phase transitions, solid lines are of the first order. The fraction $f$ label magnetization plateaus, and $c - f$ are canted (noncollinear) states deriving from them [62].
4.1.3 Further neighbor interactions and anisotropy in a triangular lattice antiferromagnet

Here, we discuss further neighbor interactions in a triangular lattice antiferromagnet. As already described in § 1.2, a noncollinear incommensurate (IC) magnetic structure is realized in a classical J1-J2 1D chain when |J1/J2| < 4. In the classical triangular lattice, an isotropic IC magnetic structure with propagation vector \( \mathbf{Q} = (q, q, 0) \) in hexagonal representation is stable by the competition between the nearest-neighbor exchange interaction \( J \) and further neighbor interactions (\( J' \) and \( J'' \)) [see Fig. 50(a)], and the 120° spin structure (\( q = 1/3 \)) is no longer the ground state [85]. The wave vector \( q \) of the IC state depends on the parameters \( J'/J \) and \( J''/J \).

Using Monte-Carlo simulation, spin-wave calculations and variational techniques, Fishman et al. investigated the change of the spin structure by the external magnetic field and the easy axis anisotropy [63]. The spin Hamiltonian in magnetic fields along the \( z \) direction (easy-axis direction) is written as,

\[
\mathcal{H} = \frac{1}{2} \sum_{<ij>} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + D \sum_i S_i^z + 2 \mu_B H \sum_i S_i^z. \tag{82}
\]

In the present system, they predict the realization of various magnetic phases shown in Figs. 50(a)~(i). Figures 50(j) and (k) show the magnetic phase diagrams as a function of the external field and anisotropy for two different sets of parameters \( J'/J \) and \( J''/J \). The phase diagrams are remarkably complex. The easy-axis anisotropy \( D \) favors the collinear states sketched in Figs. 50(a)~(f). With increasing anisotropy \( D \), the IC phase eventually transforms into the 4-sublattice (4SL) state [see Fig. 50(b)] at zero field. As the magnetic field is increased, these systems show many phase transitions when \( D \) is comparatively large. Moreover, the difference between the phase diagrams (j) and (k) arises from the change of the ratio of exchange constants \( J'/J \) to \( J''/J \).

These suggest that the competition between exchange interactions, magnetic field and easy axis anisotropy brings about remarkably rich magnetic phases. Furthermore, in such a system with distant exchange interactions, the observation of the successive phase transitions in a magnetic field is expected in real materials.
Figure 50: (a) 3-sublattice (3SL), (b) 4-sublattice (4SL), (c) 5-sublattice (5SL), (d) collinear (CL-5ii), (e) CL-7, and (f) CL-30 phases. Open and closed circles indicate up and down spins, respectively. (g) Noncollinear (NC) phases with 3 and 5 SLs, and (h) spin-flop (SF)-1 and (i) SF-2 phases. The SF-1 phase can be written \( S(R) = S(\sin \theta \cos \phi(R), \sin \theta \sin \phi(R), \cos \theta) \) where the tilting angle \( \theta \) is a constant, but the azimuthal angle \( \phi(R) = q_1 x \) varies linearly with \( x \). The SF-1 state has the wave vector \( Q = (q_1, 0) \) and two variational parameters \( (q_1, \theta) \). The SF-2 state has a 5-SL period along the \( x \) axis with tilting angles \( \theta_1 = 0, \theta_2 = 2\pi - \theta_3, \) and \( \theta_3 = 2\pi - \theta_4 \). The SF-2 state is incommensurate along the \( y \) axis with azimuthal angle \( \phi(R) = q_2 x \), wave vector \( Q = (4/5\pi, q_2) \), and three variational parameters \( (q_2, \theta_2, \) and \( \theta_3) \). (j) and (k) magnetic phase diagrams of magnetic field \( (H) \) versus easy axis anisotropy \( (D) \) for two sets of \( J'/|J| \) and \( J''/|J| \) parameters [63].
4.1.4 Multiferroic materials

Multiferroic materials have both (anti)ferromagnetic and ferroelectric properties, in which the magnetoelectric (ME) effect, i.e., generation of electric polarization by a magnetic field or magnetization by an electric field, can be realized. The ME effect in the real material, Cr$_2$O$_3$, was conjectured theoretically by Dzyaloshinsky in 1959 [64] and soon confirmed experimentally by Astrov in 1960 [65]. After this discovery, the ME effect was studied intensively in the 1960s and 1970s aiming for applications such as a multiple-state memory device. However, most of early multiferroic materials have separately magnetic and electric phase transitions, which means that the origins of these transitions have almost no relation between magnetism and ferroelectricity [66]. Since such materials have only weak ME couplings, the interest in practical applications had gradually waned off. About six years ago, a new class of multiferroic materials with a giant magnetoelectric (ME) effect, which means a spontaneous electric polarization by a magnetic field or a spontaneous magnetization by an electric field, were found in perovskite-type rare-earth manganites, TbMnO$_3$ and DyMnO$_3$ [67, 68]. These discoveries have encouraged interests in the possibility of their applications. This cross correlation allows an additional degree of freedoms in device design. By the same token, studies on the fundamental physics and microscopic origins have attracted much attention. A characteristic property of these multiferroic materials is the simultaneous occurrence of a ferroelectric and a magnetic orders accompanying with a noncollinear spiral spin configuration. Since the spiral magnetic order often arises from a competition of interactions, frustrated spin systems are promising candidates for this class of multiferroic materials. On the basis of this strategy, several new multiferroic materials with spiral spin structures have been found in the past several years, for example R$\text{Mn}_2$O$_5$ (R = Tb, Dy, and Tm) [69, 70, 71], spinel chromate CoCr$_2$O$_4$ [72], huebnerite MnWO$_4$ [73]. As well as above 3D systems, 2D triangular-lattice $\text{ACrO}_2$ ($\text{A} = \text{Cu, Ag}$) [74], CuFeO$_2$ [75], and RbFe(MoO$_4$)$_3$ [76], and 1D spin-chain cuprate LiCu$_2$O$_2$ [77] and LiCuVO$_4$ [78] have been found to be such multiferroic materials.

As typified by R$\text{MnO}_3$ (R = Tb and Dy), most of multiferroic materials with spiral spin structures have been clarified to show a cycloidal ordering in the ground states, where the plane of the spiral is parallel to the magnetic modulation vector as shown in Fig. 51(a). A microscopic mechanism of the spiral-spin-driven ferroelectrics in the cycloidal ordering was proposed by Katsura and coworkers [79]. They considered that a spin current, defined by $\textbf{S}_i \times \textbf{S}_{i+1}$, is induced between noncollinearly coupled spins, leading to local electric polarization $\textbf{P}$ given by the following equation,

$$\textbf{P} = \gamma (\textbf{S}_i \times \textbf{S}_{i+1}) \times \textbf{e}_{i+1},$$  (83)

where $\gamma$ is a constant related to the spin-orbit coupling and superexchange interactions, and $\textbf{e}_{i+1}$ is a unit vector along the magnetic modulation vector. This can be regarded as an inverse effect of the antisymmetric Dzyaloshinsky-Moriya (DM) interaction where two noncollinearly coupled magnetic moments displace the oxygen intervening between them through the electron-lattice interaction [80]. A finite electric polarization can appear when adjacent spins are coupled noncollinearly in a spiral manner and the spin rotation axis is not parallel to the magnetic modulation vector. The direction of the induced electric polarization can be reversed by reversal of spin helicity.

Some of other multiferroic materials with spiral spin structures were found to show proper-screw ordering [75, 74], where the plane of the spiral is perpendicular to the
magnetic modulation vector as shown in Fig. 51(b). The appearance of finite electric polarization in this ordering cannot be explained by the spin-current model and the inverse DM model. Recently, Arima proposed the possibility of ferroelectricity in monoclinic (or rhombohedral) crystals with the proper-screw ordering [81]. He pointed out that the removal of the mirror symmetry in a monoclinic system by the proper-screw ordering produces a spontaneous polarization. This indicates that any spiral spin structure can induce finite electric polarization on the low-symmetry lattices.

Figure 51: (a) cycloidal and (b) screw spiral orderings on one dimensional chain. The orange large arrows indicate the spontaneous electric polarization.
4.2 Physical properties of CuFe\textsubscript{1-x}Ga\textsubscript{x}O\textsubscript{2}

4.2.1 Crystal structure

CuFeO\textsubscript{2} is one of the stable compositions in the Cu-Fe-O ternary system, which was historically the first known compound exhibiting the so-called ABO\textsubscript{2} delafossite structure. ABO\textsubscript{2} where A is a monovalent cation and M is a trivalent cation, have been considered as one of the triangular lattices. Many kinds of ABO\textsubscript{2} compounds are listed by the combination of A\textsuperscript{+} (Na\textsuperscript{+}, Ag\textsuperscript{+}, Cu\textsuperscript{+}, H\textsuperscript{+}) and B\textsuperscript{3±} (Fe\textsuperscript{3+}, Cr\textsuperscript{3+}, V\textsuperscript{3+}, Al\textsuperscript{3+}, Ga\textsuperscript{3+}, Rh\textsuperscript{3+}) ions. CuFeO\textsubscript{2} belongs to a rhombohedral system with R\textsubscript{3}m symmetry, and the lattice constants are a=3.0345 Å and c=17.166 Å [82] at room temperature. As shown in Fig. 52, each element forms a triangular lattice and stacks along the [001]-direction in the sequence Fe-O-Cu-O-Fe. The magnetic properties are dominated by Fe\textsuperscript{3+} ions with S = 5/2 (3d\textsuperscript{5}) spins forming a triangular-lattice. Since Fe\textsuperscript{3+} ions with 3d\textsuperscript{5} high spin configuration have no orbital angular momentum, this is usually regarded as a Heisenberg-type spin system.

![Crystal structure of CuFeO\textsubscript{2}](image)

Figure 52: Crystal structure of CuFeO\textsubscript{2}. 

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4.2.2 Magnetic susceptibility and specific heat

When the temperature is decreased, CuFeO₂ exhibits two successive phase transitions at $T_{N1} = 14$ K, $T_{N2} = 11$ K at zero field [83]. The low-temperature specific heat of CuFeO₂ single crystal [see Fig. 53] shows a remarkable difference between the two magnetic phase transitions [84]. The first transition at $T_{N1} \sim 14$ K is marked by a broad peak in the specific heat. The second transition at $T_{N2} \sim 11$ K is accompanied by a much sharper, more intense peak. The inset shows the temperature dependence of the magnetic entropy, calculated as $S_M(T) = \int_0^T C/T \,dT$. The dashed line indicates the maximum magnetic entropy $R \ln(2S+1) = 14.90$ J mol⁻¹ K⁻¹ for $S = 5/2$.

![Figure 53: Low-temperature heat capacity of CuFeO₂ single crystal. Solid line is a guide for the eye. The inset shows the temperature dependence of the magnetic entropy [84].](image)

Magnetic susceptibilities of CuFeO₂ (Fig. 54 [85]) follow the Curie-Weiss law at high temperatures with negative Weiss temperature $\Theta \sim 88$ K [86], indicating that the dominant interaction is antiferromagnetic. This system is regarded as a frustrated magnetic system because these ordering temperatures are sufficiently low as compared to the absolute value of the Weiss temperature $\Theta$. 

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Since Fe$^{3+}$ ions with 3$d^5$ high spin configuration have no orbital angular momentum, this is usually regarded as a Heisenberg-type spin system. The ground state in such a Heisenberg triangular-lattice antiferromagnet is believed to have a noncollinear three-sublattice 120° spin configuration. Indeed, magnetic structures were determined to be the 120° spin configuration in RbFe(MoO$_4$)$_2$ [87] and Rb$_4$Mn(MoO$_4$)$_3$ (Mn$^{2+}$: 3$d^5$, S=5/2) [88], which are typical Heisenberg triangular-lattice antiferromagnets. Furthermore, other delafossites such as LiCrO$_2$ [89], CuCrO$_2$ [90, 91], and AgCrO$_2$ [92](Cr$^{3+}$: 3$d^3$, S=3/2) exhibit noncollinear spin structures and can be explained by Heisenberg-type spin systems. On the contrary, CuFeO$_2$ exhibits an Ising-like 4-sublattice (4SL) (1↑1↓1↑1↓) collinear order below $T_{N2}$ [85, 83]. As shown in Fig. 55 (a), the magnetic moments are pointed along the [001] direction.

As the temperature is decreased, CuFeO$_2$ shows a transition from a paramagnetic phase to an intermediate(IM) state one with a sinusoidally modulated incommensurate spin structure at $T_{N1}$ =14 K [see Fig. 55 (b)]. In this incommensurate structure, the spins align, to be collinear along the [001] direction, with sinusoidal modulation of these amplitudes characterized by the propagation wave vector $Q = (q,q,3/2)$, with $q$ ~ 0.2 [93]. Then the transition to the commensurate 4-sublattice ground state occurs at $T_{N2} = 11$ K.

Moreover, one of the most fascinating physical properties of CuFeO$_2$ arises below $T_{N2}$ when a finite external magnetic field is applied to the [001] direction. The magnetic field ($H$) - temperature ($T$) phase diagram obtained below $H = 14$ T is shown in Fig. 56 [75]. Several successive field-induced phase transitions take place as shown in Figs. 55 [94, 95]. CuFeO$_2$ has shown to exhibit magnetic phase transitions at $H_{c1} \approx 7$ T, $H_{c2} \approx 13$ T, $H_{c3} \approx 20$ T, $H_{c4} \approx 34$ T and $H_{c5} \approx 53$ T. For $H_{c1} < H$
< $H_{c2}$, a ferroelectric and incommensurate (FEIC) order was observed [see Fig. 55 (c)] [96]. Since the occurrence of a spontaneous electric polarization was reported in the FEIC phase, CuFeO$_2$ has attracted renewed interest as one of the multiferroic materials [75]. It was observed in CuFeO$_2$ a five-sublattice (5SL) ($\uparrow\uparrow\uparrow\downarrow\downarrow$) collinear state where the spins again align parallel to the [001] direction for $H_{c3} < H < H_{c4}$ [see Fig. 55 (d)] [96, 84]. Magnetic structures at higher magnetic fields above $H_{c3}$ have not yet been experimentally determined. However, on the basis of magnetization with a $1/3$ plateau and a linear increase above the plateau region, the magnetic structures in the high-field magnetic phases were suggested to be a collinear three sublattice (3SL) ($\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\downarrow$) state for $H_{c3} < H < H_{c4}$, and a canted three-sublattice (C3SL) state for $H_{c4} < H < H_{c5}$ [see Figs. 55(e) and (f)]. Above $H_{c5}$, it was argued that an umbrella structure with a cone-type spin configuration (Cone) is realized [see Fig. 55(g)] [95, 97, 98]. However, its curious magnetic ordering and field-induced transitions are still under intensive debate.

Figure 55: Magnetic structure of CuFeO$_2$. (a) 4-sublattice (4SL), (b) Intermediate, (c) ferroelectric incommensurate (FEIC), (d) 5-sublattice (5SL), (e) 3-sublattice (3SL), (f) canted 3-sublattice (C3SL) and (g) cone spin structures.
Figure 56: Temperature versus magnetic field phase diagram of CuFeO$_2$ with $H$ applied along the [001] axis. Open and filled symbols represent the data points in the cooling (or $H$-decreasing) and warming (or $H$-increasing) runs, respectively. Diamond, square, triangle, and inverse triangle data points were obtained from measurements of magnetization, dielectric constant, electric polarization, and magnetostriction, respectively [75].

Recently, significant findings were reported from synchrotron x-ray diffraction studies. The crystal symmetry lowers from a rhombohedral to a monoclinic one with $C2/m$ space group below $T_{N1}$ and then to a much lower symmetry monoclinic one below $T_{N2}$, as shown in Figs. 57(a) and (b) [99]. In previous studies, a lattice distortion was also reported to occur with the field-induced magnetic phase transitions [99, 100, 101, 102] as shown in Fig. 57(c) [101]. These behaviors imply an important role of spin-lattice coupling in inducing phase transitions in CuFeO$_2$. Through spin-lattice coupling, changes in the magnetic interactions due to lattice distortion occur as mentioned in § 4.1.2. Then, it was suggested that these magnetic structures were explained by alteration of exchange interactions with the lattice distortion. Recent theories suggested that competition between second and third neighbor exchange interactions ($J''$, $J'''$), biquadratic exchange, and trigonal anisotropy play an important role in magnetic properties of CuFeO$_2$ and the strong spin-lattice coupling(c) largely affects magnetic behavior of CuFeO$_2$. Therefore, various magnetic phases are realized and interesting phenomena, such as multiferroics and magnetization plateaus, were found out in CuFeO$_2$.

It is important to note that, as Mekata et al. [85] suggested, the classical ground state of a 2D Heisenberg triangular lattice antiferromagnet with relatively large next and third nearest neighbor interactions is not a 120° spin structure but an incommensurate spiral one characterized by $Q = (q,q)$, with $q \sim 0.2$. The wave vector is in good agreement with that of the IM state ($Q = (q,q,3/2)$, with $q \sim 0.2$). On the other hand, a successive phase transition is known to occur in a Heisenberg triangular lattice antiferromagnet with weak axial anisotropy. In a system with a nearest neighbor interaction, a peculiar collinear phase, in which only the longitudinal spin component of a 120°...
Figure 57: (a) Fractional changes in the lattice parameters of $a'$, $b'$, and $c$ measured for increasing and decreasing temperatures. Here, for instance, $\Delta a' = (a(T) - a(20K))/a(20K)$. Open and closed symbols denote the data for temperature increasing and decreasing processes, respectively [99]. (b) Example of lattice distortion in CuFeO$_2$ at low temperatures. (c) Magnetic field dependence of the lattice constants $a$ (squares) and $b$ (circles) at $T = 4.2$ K. The magnetic field is applied along the the $[001]$ axis. [101].

spin structure ($q = 1/3$) parallel to the easy-axis direction undergoes ordering whereas the transverse components remain disordered, appears in the intermediate temperature region [103]. We suggest that a similar intermediate phase appears in CuFeO$_2$; i.e., it is considered that the sinusoidal collinear spin structure in $T_{N2} < T < T_{N1}$ corresponds to an ordering of the $[001]$ axis (easy-axis direction in CuFeO$_2$) component of the incommensurate spiral spin alignment with $q \sim 0.2$. Then, if the spin-lattice coupling is less significant, the system undergoes full spiral ordering with further decreases in temperature. However, the significant lattice distortion was reported to occur below $T_{N2}$, as shown in Figs. 57(a). The strong spin-lattice coupling in CuFeO$_2$ is considered to bring this material into a collinear 4SL ordering below $T_{N2}$. 

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4.2.4 Effect of non-magnetic ion substitution

Furthermore, fascinating physical properties were also observed when the magnetic Fe$^{3+}$ ions were replaced by tiny amounts of non-magnetic ions. The change of magnetic phases caused by substitution of nonmagnetic ions such as Al$^{3+}$, Rh$^{3+}$ and Ga$^{3+}$ for Fe$^{3+}$ has been studied [104, 105, 106, 107, 108]. Figure 58(a) shows temperature versus Ga content $x$ magnetic phase diagram [109]. The spin structures in the phase diagram are shown in Figs. 58(b)~(e). The $H_{c1}$ is reduced with increasing the content of nonmagnetic Ga ions. As a result, the FEIC phase can be induced at zero magnetic field by a certain amount of nonmagnetic ions. Moreover, the ground state is changed into an oblique partial disordered state, where spins are tilted by about 50° from the [001] direction toward the ⟨110⟩ direction, with further substitution [110]. This result indicates that the ferroelectric phase becomes stable, and this phase can be expanded by the substitution of nonmagnetic ions. However, the origin of the expansion of the FEIC state by doping of nonmagnetic ions is still unclear.

![Figure 58: (a) Temperature versus Ga concentration $x$ magnetic phase diagram of CuFe$_{1-x}$Ga$_x$O$_2$ [109]. (b) Intermediate, (c) oblique partial disorder, (d) 4-sublattice and (e) ferroelectric incommensurate state in CuFe$_{1-x}$Ga$_x$O$_2$.](image-url)
4.3 Synthesis and characterization

4.3.1 Crystal growth

Single crystal samples of CuFe$_{1-x}$Ga$_x$O$_2$ ($x = 0.000 \sim 0.028$) used in this work were grown by a floating zone (FZ) technique. The reason why we choose Ga$^{3+}$ ions as nonmagnetic ions is that the radius of Ga$^{3+}$ ion (0.62 Å) is close to that (0.64 Å) of Fe$^{3+}$ ion. Therefore, structural distortion due to the substitution must be small compared to the others (Al$^{3+}$: 0.51 Å and Rh$^{3+}$:0.67 Å).

As starting materials, powders of Cu$_2$O [4N (99.99 % pure)], Fe$_2$O$_3$ (3N) and Ga$_2$O$_3$ (4N) were well mixed in the molar ratio 1:1-x:x and filled into an alumina boat which was introduced into a tube furnace [see Fig. 59(a)]. The solid state reaction between Cu$_2$O, Fe$_2$O$_3$ and Ga$_2$O$_3$ was carried out at 900 °C for 24 hours in a flow of argon gas [see Fig. 59(b)]:

$$\text{Cu}_2\text{O} + (1-x)\text{Fe}_2\text{O}_3 + x\text{Ga}_2\text{O}_3 \rightarrow \text{CuFe}_{1-x}\text{Ga}_x\text{O}_2. \quad (84)$$

The X-ray powder diffraction technique was used to confirm that the synthesized powder was CuFe$_{1-x}$Ga$_x$O$_2$ and to check for the presence of extrinsic or impurity phases. The cylindrical feed rods of about 4 ~ 5 mm in diameter and 45 ~ 80 mm in length were made from the synthesized CuFe$_{1-x}$Ga$_x$O$_2$ powder under the hydrostatic pressure of 200 atm and then sintered again in argon at 900 °C for 5 hours to increase the density of the rods [see Fig. 59(c)].

Figure 59: (a) Sample setting inside a tube furnace. (b) Reaction process of CuFe$_{1-x}$Ga$_x$O$_2$ powder. (c) Process to prepare sintered rods.
Single crystal growth was carried out by a zone melting method with an infrared image furnace, as sketched in Fig. 60 [111, 112]. The feed rod was suspended from the upper holder by a nickel wire and the lower seed, made from a sintered rod, was fixed by a chuck. The growth was started by melting the tips of the two rods which were then brought together to form a molten zone. The feed and the seed were rotated at 20 rpm separately in opposite directions in order to promote the stirring of the melt and to equalize the heat in flow. Crystal growth was carried out with a flow of argon gas and at a growth rate in the range of 1 mm/h. As-grown crystals are 4 ~ 5 mm in diameter and 15 ~ 50 mm in length. One of the typical single crystals grown with this furnace is shown in Fig. 61.

Figure 60: (a) Illustration of infrared image furnace for crystal growth. (b) Schematic view of crystal growth.

Figure 61: Synthesized single crystal of CuFe_{1-x}Ga_xO_2
4.3.2 Sample characterization

Figure 62 shows the X-ray powder diffraction patterns of the pulverized samples from single crystals of CuFe$_{1-x}$Ga$_x$O$_2$ for designated $x$. In each sample, any impurity phase was not observed, and the single crystal is in a single phase. All the diffraction peaks can be indexed by the delfossite structure, which confirms that the structure of each synthesized crystal is that of the hexagonal CuFeO$_2$.

![X-ray diffraction patterns](image)

Figure 62: X-ray powder diffraction patterns for the pulverized samples of CuFe$_{1-x}$Ga$_x$O$_2$ and calculated patterns.

We also determined all the crystal axes by back-reflection Laue method as shown in Figs. 63. We took Laue photographs in the arrangement depicted in Fig. 63(a). The Laue photograph of the sample was compared with the Laue pattern simulated figure as shown in Figs. 63(b) and (c). For all the compounds, the crystallographic [001] direction was naturally at the direction of 0 ~ 20 ° tilted from the growth direction. The observed pattern has a hexagonal symmetry and almost all reflection spots are undistorted, which identifies that the grown CuFe$_{1-x}$Ga$_x$O$_2$ is a single crystal with good crystallinity.

We also determined Ga content with an inductively coupled plasma - atomic emission spectrometer (ICP-AES). In ICP-AES, induced electric field is generated by sending high frequency current through the induction coil twisted around the discharge tube (torch), and argon gas is introduced there to make the plasma state as shown in
Fig. 63. (a) Arrangement of Laue photograph. (b) Laue photograph of a single crystal of CuFe$_{1-x}$Ga$_x$O$_2$ in the view from the [001] axis. (c) Simulated Laue pattern in the view from the [001] axis.

Fig. 64. If a spray of the solution sample is introduced into argon plasma, the metallic elements and the metalloid element in the solution are excited with 6000-7000 °C heat. Then, when each excited state returns to the ground state, the light of a wavelength peculiar to each element is emitted. By detecting this emission line, qualitative and quantitative analysis can be carried out from a wavelength and luminescence intensity, respectively. In the measurements, about 5 mg of CuFe$_{1-x}$Ga$_x$O$_2$ samples (the measuring object) were melted in 10 ml of hydrochloric acid in order to ionize, and 90 ml of ultrapure water was added. The concentrations of each ions in the sample were determined as compared with the five reference solutions including blank solution as shown in Figs. 65. Ga content $x$ of the sample is given as $\frac{\text{Ga content (ppm)}/M_{\text{Ga}}}{\left(\frac{\text{Ga content (ppm)}/M_{\text{Ga}}}{\text{Fe content (ppm)}/M_{\text{Fe}}}\right)}$, where $M_{\text{Ga}} = 69.723$ and $M_{\text{Fe}} = 55.845$ are atomic weights of Ga and Fe, respectively. We determined the Ga content $x$ of all the samples using the above formula. By investigating the Ga content of some parts in each crystal, the error bar of $x$ was only about ±0.0005.
Figure 64: Schematic view of inductively coupled plasma - atomic emission spectrometer (ICP-AES)

Figure 65: Examples of inductively coupled plasma - atomic emission spectrometry ($x = 0.008$). Concentration (ppm) dependence of spectral intensity for (a) Cu, (b) Fe and (c) Ga.
4.4 Experimental results

4.4.1 Magnetization and electric polarization

Figure 66(a) shows the magnetization curve of CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ at 4.2 K in pulsed magnetic fields of up to 22 T along the [001] direction. We observed step-like increases at about $H_{c1} \simeq 7$ T, $H_{c2} \simeq 13$ T and $H_{c3} \simeq 21$ T. Since all the magnetic transitions at $H_{c1}$ (4SL$\rightarrow$FEIC), $H_{c2}$ (FEIC$\rightarrow$5SL) and $H_{c3}$ (5SL$\rightarrow$3SL) in the figure have large hysteresis, these must be first-order phase transitions. Here, we define the transition fields in the field ascending process. Figures 66(b), (c), and (d) depict the magnetization curves of CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.001$, 0.013 and 0.028, respectively, at the same conditions as in the $x=0.000$ sample. The transitions broaden with increasing $x$.

We observed spontaneous electric polarization of CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ at 4.2 K for $H//[001]$ as shown in Fig. 66(e), which is similar to that in previous reports measured in pulsed magnetic field [12, 13]. The magnitude of spontaneous electric polarization for the field ascending process is $\sim 100 \mu$ C/m$^2$ in our pulsed field case, while those were reported to be $250 \sim 400 \mu$ C/m$^2$ in static magnetic fields [75, 105]. This must be caused by the difference of alignment of electrically polarized domains in the samples with different field sweep rates. We also observed the difference of the magnitudes of the spontaneous electric polarization between field ascending and descending processes, and a small spontaneous polarization in the field-ascending process above $H_{c2}$.

The field dependences of the electric polarization of CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.001$, $x = 0.013$ and $x = 0.028$ at 4.2 K for $H//[001]$ are shown in Figs. 66(f), 66(g) and 66(h). With increasing the content of Ga$^{3+}$ ions, the magnitude of spontaneous electrical polarization increases and the difference of magnitude of the spontaneous electric polarization between field ascending and descending processes decreases. We also observed the rapid shift of $H_{c1}$ and the expansion of ferroelectric field region by doping of Ga$^{3+}$ ions. Figure 67 shows the magnetization curve of CuFe$_{1-x}$Ga$_x$O$_2$ at 2 K in stable magnetic fields of up to 7 T along the [001] direction. Eventually, the 4SL phase disappears completely and is replaced by the FEIC phase for $x = 0.028$ at 4.2 K. In a previous paper [107], the boundary between the 4SL and the FEIC phases was reported to be $x=0.016 \sim 0.020$. Obviously, the shift of $H_{c1}$ differs from those of other transition fields, when magnetic Fe$^{3+}$ ions are replaced by non-magnetic Ga$^{3+}$ ions.
Figure 66: Comparison of the field dependences of (a)-(d) magnetization and (e)-(h) electric polarization of CuFe$_{1-x}$Ga$_x$O$_2$ with the designated $x$ at 4.2 K for $H//\{001\}$. The large arrows along the magnetization and electric polarization curves in the figures indicate the field sweep directions. The solid and broken lines are field ascending and descending processes, respectively. The transition fields $H_{c1}$, $H_{c2}$, $H_{c3}$, and $H_{c3'}$ are defined for the field-ascending process.
Figure 67: Comparison of magnetization curves of CuFe$_{1-x}$Ga$_x$O$_2$ with different Ga$^{3+}$ contents at 4.2 K for $H||[001]$ in magnetic fields of up to 7 T. The curve shifts up by 0.05 $\mu_B$/Fe$^{3+}$ as increasing $x$.

The change of magnetization curves of CuFe$_{1-x}$Ga$_x$O$_2$ with various Ga$^{3+}$ content $x$ in magnetic fields of up to 50 T along the [001] direction at 4.2 K is demonstrated in Fig. 68. We observed several successive field-induced phase transitions for $x = 0.000$, which are in good agreement with those in previous works. Since the magnetic transitions at $H_{c4}$ (3SL to C3SL phase transition) have no hysteresis, this magnetic transition must be a second-order phase transition. On the other hand, hysteresis was observed at $H_{c5}$ (C3SL→Cone phase), suggesting a first-order phase transition. In our results on magnetization curves of CuFe$_{1-x}$Ga$_x$O$_2$, new phase between 5SL and 3SL phases was clearly observed for the cases of $x = 0.013$ and 0.028. This fourth field-induced (4th-FI) phase is expanded by increasing the content of Ga$^{3+}$ ions. Since there is clear hysteresis near the new magnetic transition at $H_{c3'}$ (5SL to 4th-FI phase), this magnetic transition must be a first-order phase transition. We have found that the step-like magnetization jumps associated with the phase transitions become small and the slopes of magnetization curves in the spin-collinear plateau phases increase with increasing $x$.

It is shown in Fig. 69 the phase diagram of magnetic field ($H$) versus Ga$^{3+}$ content ($x$) in which the phase boundaries are determined by the magnetization measurements at 4.2 K and 2 K. We defined the peak positions of the field derivative of magnetization curves ($dM/dH$) in the field ascending process as the critical fields $H_{c1}$, $H_{c3}$, $H_{c3'}$, $H_{c5}$, and $H_{c5}$. The critical field $H_{c4}$ was determined by the inflection point of $dM/dH$. This figure clearly shows that the FEIC phase is expanded rapidly with the
substitution of nonmagnetic Ga$^{3+}$ ions for Fe$^{3+}$ ions as described above. $H_{c2}$, $H_{c3}$, $H_{c4}$ and $H_{c5}$ decrease with the increase of $x$, although their shifts are small. In contrast, the transition field $H_{c3}$ increases, and the 3SL phase narrows with increasing the Ga content.

Figure 68: Comparison of magnetization curves of CuFe$_{1-x}$Ga$_x$O$_2$ with different Ga$^{3+}$ contents at 4.2 K for $H_{||}[001]$ in magnetic fields of up to 52 T. Each curve is separated from the nearest curve by 0.5 $\mu_B$/Fe$^{3+}$ at zero field. Thick and thin lines are field ascending and descending processes, respectively. Dashed arrows indicate the changes of the transition fields of the magnetization curves for the field ascending process.
Figure 69: Magnetic field versus Ga content $x$ phase diagram for $H\parallel[001]$ in CuFe$_{1-x}$Ga$_x$O$_2$. The boundaries of the phases are determined from the transition fields of $H_{c1}$, $H_{c2}$, $H_{c3}$, $H_{c3'}$, $H_{c4}$, and $H_{c5}$ in Fig. 65. The figure in each phase shows the observed or expected spin structure, and the letters such as 4SL and FEIC are explained in the text.
4.4.2 Multi-frequency ESR

Figures 70(a) and 70(b) show the frequency dependences of ESR absorption spectra of CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ [113] and $x = 0.012$, respectively, for $H \parallel c$ at 1.6 K. The resonance fields are indicated by downward arrows in Figs. 70 and are plotted with red filled circles ($x=0.000$) and blue filled triangles ($x=0.012$) on the frequency-field plane as shown in Fig. 71. The resonance branches for the $x = 0.012$ sample slightly shift to the low frequency side compared with those for the $x = 0.000$ sample. The lowest resonance mode at zero field changes only about 15 GHz, and the shift of the magnetic field corresponding to this frequency change is only about 0.5 T. On the contrary, the ESR linewidth changes drastically with the increase of $x$. The linewidth broadens largely with increasing $x$ in CuFe$_{1-x}$Ga$_x$O$_2$.

![Figure 70: Frequency dependence of ESR absorption spectra of CuFe$_{1-x}$Ga$_x$O$_2$ with (a) $x = 0.000$, and (b) $x = 0.012$ for $H \parallel c$ at 1.6 K. The arrows indicate ESR absorption points, namely resonance fields. The vertical dotted line indicates the transition field $H_{c1}$](image-url)
Figure 71: Frequency versus magnetic field plot of the resonance fields of CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ and $0.012$ at 1.6 K for $H//\langle001\rangle$. Closed circles and triangles denote the ESR resonance fields observed in CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ and $0.012$, respectively. We found a small frequency shift of the excitation modes by Ga doping.

In order to clarify this broadening of the linewidth, we demonstrate the $x$ dependence of the ESR spectra at $\sim$200 GHz on the lowest excitation branch as shown in Fig. 72. In this figure, the center of the horizontal axis indicated as 0 T is the resonance field. Here, we define the linewidth of the spectrum as a half of the full field width from the maximum of the spectrum to the baseline as indicated by $2\Delta H_{ESR}$ with a double-pointed arrow. The linewidths $\delta H_{ESR}$ for the $x = 0.000$ and $x = 0.012$ samples are about 0.2 T and 2.0 T, respectively.

We also performed multi-frequency ESR measurements on the $x = 0.013$ sample, but the ESR signal was not observed below 7 T. We believe that no ESR signal for the $x = 0.013$ sample would be caused by a large line broadening. As described in Ref. [113], no clear ESR signal was observed in the FEIC state ($H_{c1} < H < H_{c2}$). In addition, pulsed field ESR measurements on CuFe$_{1-x}$Ga$_x$O$_2$ were carried out in order to detect ESR signals above $H_{c2}$. Although some signals with the line width of $\sim$ several T were observed, it is difficult to assign the ESR excitation modes correctly. Therefore, we analyze the ESR resonance branches in the 4SL state.
Figure 72: Ga content $x$ dependence of ESR spectra at $\sim$200 GHz and 1.6 K for $H // [001]$. The center of the horizontal axis indicated as 0 T corresponds to the resonance field position of each spectrum.
4.5 Analyses

First, we analyze the frequency dependence of the ESR resonance fields for \( H \parallel [001] \). As described in § 4.2.3, this system cannot be explained by a simple Heisenberg equilateral triangular lattice antiferromagnet. It's believed that a spin-lattice coupling and a small anisotropic term play an important role in stabilizing the collinear 4SL magnetic structure. In this study, we start from the Hamiltonian and assume that the [001] direction is the \( z \) direction.

\[
\mathcal{H} = \sum_{<ij>} J_{ij} \mathbf{S}(r_i) \cdot \mathbf{S}(r_j) + D \sum_i (\mathbf{S}(r_i))^2 + E \sum_i \{(\mathbf{S}(r_i))^2 - (\mathbf{S}^\parallel(r_i))^2\} - g_z \mu_B \sum_i \mathbf{S}(r_i) \cdot \mathbf{H},
\]

where \( J_{ij} \) is the antiferromagnetic exchange constant between spins at the \( i \)- and \( j \)-sites, \( \sum_{<ij>} \) the summation over pairs of the spins, \( \mathbf{S}_i \) \( S = 5/2 \) spin operator of \( \text{Fe}^{3+} \) at the \( i \)-th site, \( D \) and \( E \) the uniaxial and rhombic anisotropic constants, \( g_z \) the \( g \)-value of \( \text{Fe}^{3+} \) spin along the \( z \)-axis, \( \mu_B \) the Bohr magneton and \( H \) the external magnetic field along the \( z \)-axis.

Recent theoretical studies pointed out that strong spin-lattice couplings favor a collinear magnetic ordering. \([62, 114]\) The strong spin-lattice coupling may explain the observed 4SL spin structure in \( \text{CuFeO}_2 \). As already mentioned, synchrotron X-ray diffraction measurements suggested that the crystal undergoes a structural phase transition from hexagonal \( R3m \) to a lower monoclinic symmetry with a scalene triangular lattice distortion below \( T_{N2} \) \([99]\) as shown in Fig. 73(a). This indicates an important role of spin-lattice couplings in magnetic structure of \( \text{CuFeO}_2 \). From these reasons, the spin-lattice couplings stabilize the 4SL structure in this system. Through spin-lattice coupling, changes in the magnetic interactions due to lattice distortion occur. Hence, we assume three kinds of antiferromagnetic nearest-neighbor exchange constants, \( J_1 \), \( J_2 \), and \( J_3 \). From the view point of the magnetic structure, the smallest \( J_3 \), which is the exchange interaction between the spins pointed along the same direction [see Fig. 73(b)], stabilizes the 4SL structure. In addition, the second and the third-nearest-neighbor intraplane constants \( J' \) and \( J'' \), and the nearest-neighbor interplane one \( J_z \) are included in our analysis (see Figs. 73(b) and (c)). In the recent inelastic neutron scattering experiments, such distant exchange interactions are necessary to explain the energy dispersion.\([113, 115, 116, 117, 118, 119]\)

As for the anisotropic terms, only a uniaxial anisotropy \( D \), which acts to create an easy-axis anisotropy along the [001] direction, have been considered in some studies \([113, 115, 116, 117, 118, 119]\). The uniaxial anisotropy \( D \) with a negative value stabilizes the collinear magnetic structure. On the other hand, an in-plane anisotropy \( (E \) term) is necessary to explain the splitting of ESR mode around 300 GHz at zero field.
Figure 73: Magnetic structure and the details of the exchange interactions for the 4-sublattice collinear state in CuFe$_{1-x}$Ga$_x$O$_2$. (a) Lattice distortion and the nearest-neighbor exchange interactions. Owing to a distorted triangular lattice in the (001) plane at low temperatures, we assume three kinds of nearest-neighbor exchange constants, $J_1$ (thin line), $J_2$ (thick line), and $J_3$ (thin dashed line). (b) In-plane magnetic structure and the second and the third nearest-neighbor exchange constants $J'$ (thick dashed line) and $J''$ (arc-like curve). We might also assume three different $J'$ and $J''$ values, but we ignore this effect for simplicity. (c) Interplane magnetic structure and the interplane exchange interactions (dash-dotted lines). Only $J_z$ is assumed for simplicity.
We derive the resonance conditions by solving the following equation of motion,
\[ \hbar \partial S_l / \partial t = [S_l(r_i) \times H_l(r_i)] , \tag{86} \]
where \( S_l \) is a spin on the \( l \)-th sublattice located at \( r_i \). The \( r_i \) is expressed in the trigonal notation, and the lattice constants are defined as standardized unity. \( H_l \) is a mean-field applied on the \( l \)-th sublattice moment given by
\[ H_l(r_i) = -\partial H / \partial S_l(r_i) . \tag{87} \]

We utilize the following expressions, which represent the motion of the \( l \)-th sublattice moment,
\[ S_l = (\delta S_{ix} e^{-i(\omega t - k \cdot r_i)}, \delta S_{iy} e^{-i(\omega t - k \cdot r_i)}, S_l) . \tag{88} \]
where \( |\delta S_{ix}|, |\delta S_{iy}| \ll |S_l| \) and \( k = 2\pi q \).

Substituting eqs. 87 and 88 into eq. 86, we have
\[ -\hbar \omega \delta S = \tilde{M} \cdot \delta S , \tag{89} \]
where
\[ \delta S = \{\Delta S_{1x}, \Delta S_{1y}, \Delta S_{2x}, \Delta S_{2y}, \Delta S_{3x}, \Delta S_{3y}, \Delta S_{4x}, \Delta S_{4y}\} . \tag{90} \]

Theoretical spin wave resonance modes correspond to the absolute eigenvalues of \( \omega \).

The matrix \( \tilde{M} \) is given as
\[
\tilde{M} = \begin{pmatrix}
0 & A_+ & 0 & -C & 0 & -K & 0 & -B \\
A_- & 0 & C & 0 & K & 0 & B & 0 \\
0 & C & 0 & A_+ & 0 & B & 0 & K \\
-C & 0 & A_- & 0 & -B & 0 & -K & 0 \\
0 & -N & 0 & -F & 0 & A_+ & 0 & -C \\
N & 0 & F & 0 & A_- & 0 & C & 0 \\
0 & F & 0 & N & 0 & C & 0 & A_- \\
-F & 0 & -N & 0 & -C & 0 & A_+ & 0 \\
\end{pmatrix} \tag{91}
\]

where
\[ A_+ = -A - 2SE + g\mu_B HS , \tag{92} \]
\[ A_- = A - 2SE - g\mu_B HS , \tag{93} \]
\[ A'_+ = A + 2SE + g\mu_B HS , \tag{94} \]
\[ A'_- = -A + 2SE - g\mu_B HS , \tag{95} \]
\[ A = -2S(J_1 + J_2 - J_3 - J' + J'' + J_z - D) \\
-2SJ'\cos(-k_x + k_y) - 2SJ''\cos(k_x + k_y) , \tag{96} \]
\[ C = -2J_1S\cos(k_x + k_y) - 2J''S\{\cos(2k_x) + \cos(2k_y)\} \\
-2zS\cos\{(-k_x + k_y + k_z)/3\} , \tag{97} \]

96
By solving the secular equation 89, we obtain magnetic field dependence of the resonance frequencies at the zone center \( \mathbf{q} = (0 0 0) \) (ESR modes). We calculate the energy dispersion along \((h h 3/2)\) and \((2h -h 3/2)\) at zero field in order to compare with previous inelastic neutron scattering results. Here, \( \mathbf{q} = (0 0 0) \) and \((1/4 1/4 3/2)\) are magnetically equivalent in the 4SL phase. We also calculate the magnetic susceptibility \( \chi_\perp \) for \( H \perp [001] \).

The resonance modes around 600 GHz are believed to be caused not by normal magnons, which are excited by the oscillatory magnetic fields, but electromagnons [120], which are excited by the oscillatory electric field. Recently, Nakajima et al. [119] reported that the mechanism based on d-p hybridization model[81] explains the electromagnon excitations in this system. Kimura et al. argued that these higher frequency modes agree better with the calculated resonance modes at \( \mathbf{q} = (0 0 3/2) \) than those at the zone center \( \mathbf{q} = (0 0 0) \). [113] For these reasons, the analysis of higher ESR modes is omitted in this thesis.

As shown in Fig. 74, we obtain good agreement between the experiment and the calculation with the following parameters: \( J_1/k_B = 2.7 \) K, \( J_2/k_B = 3.0 \) K, \( J_3/k_B = 1.8 \) K, \( J'/k_B = 0.93 \) K, \( J''/k_B = 1.9 \) K, \( J_z/k_B = 0.59 \) K, \( D/k_B = -0.31 \) K, \( E/k_B = 0.055 \) K, and \( g = 2.00 \) for the \( x = 0.012 \) sample. With these parameters, we also reproduce the experimental value of magnetic susceptibility \( \chi_\perp = 0.057 \) \( \mu_B/T \). For the \( x = 0.000 \) sample, we use the following parameters reported in Ref. [26]: \( J_1/k_B = 3.0 \) K, \( J_2/k_B = 3.4 \) K, \( J_3/k_B = 2.0 \) K, \( J'/k_B = 1.1 \) K, \( J''/k_B = 2.2 \) K, \( J_z/k_B = 0.54 \) K, \( D/k_B = -0.33 \) K, \( E/k_B = 0.07 \) K, and \( g = 2.00 \). By using these parameters, we also reproduce the experimental value of magnetic susceptibility \( \chi_\perp = 0.051 \) \( \mu_B/T \). [113]

The energy dispersion curves at \( H=0 \) for \((h h 3/2)\) and \((2h -h 3/2)\) calculated with these parameters are shown in Figs. 75(a) and (b). (Here, \( E \) term is neglected for simplicity.) The analytical result for \( x=0.000 \) reproduces the observed energy dispersion by Ye et al. [115] [see Fig. 74(c)] comparably well. From these analyses, we insist that the energy dispersion curves do not change so much, when the 4SL phase is realized at zero field. On the other hand, it was reported that the \( D \) value changes largely in the case of \( x = 0.035 \) [118] as shown in Table 3. This result may suggest that the \( D \) value changes largely in the FEIC phase.
Table 3: Comparison of the fitting parameters in CuFe$_{1-x}$Ga$_x$O$_2$ (in K).

<table>
<thead>
<tr>
<th>x</th>
<th>$J_1/k_B$</th>
<th>$J_2/k_B$</th>
<th>$J_3/k_B$</th>
<th>$J'/k_B$</th>
<th>$J''/k_B$</th>
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<tbody>
<tr>
<td>0.000 (This study) [113]</td>
<td>3.0</td>
<td>3.4</td>
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<td>2.2</td>
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<tr>
<td>0.000 [118, 119]</td>
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<td>4.2</td>
<td>1.4</td>
<td>0.95</td>
<td>3.3</td>
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<td>3.0</td>
<td>1.8</td>
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<td>1.9</td>
</tr>
<tr>
<td>0.035 [118]</td>
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<td>3.9</td>
<td>1.5</td>
<td>1.6</td>
<td>2.3</td>
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<table>
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<tr>
<th>x</th>
<th>$J_z/k_B$</th>
<th>$J_{2z}/k_B$</th>
<th>$J_{3z}/k_B$</th>
<th>$D/k_B$</th>
<th>$E/k_B$</th>
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<tbody>
<tr>
<td>0.000 (This study) [113]</td>
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<td>-</td>
<td>-</td>
<td>-0.33</td>
<td>0.07</td>
</tr>
<tr>
<td>0.000 [118, 119]</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
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<tr>
<td>0.012 (This study)</td>
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<td>-0.08</td>
<td>-</td>
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</table>

Figure 74: Frequency versus magnetic field plot of the resonance fields of CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ and 0.012 at 1.6 K for $H//[001]$. Closed circles and triangles denote the ESR resonance fields observed in CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ and 0.012, respectively. The solid lines represent calculated resonance modes.
Figure 75: Energy dispersion curves of $\text{CuFe}_{1-x}\text{Ga}_x\text{O}_2$ with (a) $x = 0.000$ and (b) $x = 0.012$ calculated for the $(h h 3/2)$ and $(2h - h 3/2)$ directions. Filled and open circles show the spin-wave excitations for the $(h h 3/2)$ and $(2h - h 3/2)$ directions, respectively. The size of the circles represents the scattering intensity. (c) Energy dispersion curves of $\text{CuFeO}_2$ observed by Ye et al. [115]
4.6 Discussion

First, let us discuss the magnetic phase transition at $H_{c1}$ (4SL→FEIC). We observed a rapid shift of $H_{c1}$ and expansion of the FEIC phase by doping of Ga$^{3+}$ ions. We argue these findings from a viewpoint of the excitation modes. The energy minima of the dispersion curve with an energy gap $\Delta \sim 0.9$ meV appear at symmetric positions (0.21, 0.21, 3/2) and (0.29, 0.29, 3/2) against the magnetic Bragg point (0.25, 0.25, 3/2) at zero field in CuFe$_{1-x}$Ga$_x$O$_2$ with $x = 0.000$ [115]. Remarkably, these are the same wave vectors associated with the FEIC state of CuFeO$_2$ in a magnetic field and are dynamic precursors to the multiferroic phase.

The transition from the 4SL to the FEIC states can be understood as the softening of magnetic lowest excitation mode [115]. As we described in § 4.4.2, the doping of Ga$^{3+}$ ions does not bring a large effect on the shift of the lowest excitation mode, but on the line width of ESR spectra. The energy shift of the lowest excitation mode seems to be too small to explain the large shift of $H_{c1}$, which is defined by the change of the transition field $H_{c1}$ from the $x = 0.000$ value in the field ascending process of magnetization curve. Accordingly, the shift of the excitation mode of only 15 GHz (the order of 0.1 T) is not the cause of the large shift of $H_{c1}$.

As shown in Fig. 76(a), the lowest excitation mode for the $x=0.000$ sample is split in a magnetic field due to the Zeeman effect, and the energy gap $\Delta$ at the minima of the lower mode $\omega_L$ approaches zero at $H \sim H_{c1}$. The softening of the lower mode $\omega_L$ achieved by applying a magnetic field certainly reveals a close connection between the breakdown of the 4SL state and the occurrence of the field-induced FEIC order. Since the FEIC phase appears by Ga$^{3+}$ doping as well as by magnetic field, doping of Ga$^{3+}$ ions must give rise to the softening of $\omega_L$. Since the energy change of the excitation mode is very small, the parameter values can not change significantly by Ga doping in the 4SL phase. In the ascending magnetization process, the transition fields $H_{c1}$ are 7.5 T and 5.4 T for $x = 0.000$ and 0.012, respectively.

Calculated spin-wave dispersion curves for the $x = 0.012$ sample [Fig. 75(b)] do not change significantly compared with those for the $x = 0.000$ sample. The energy gap $\Delta$ at the minima of the lower mode $\omega_L$ has a finite value at $H = H_{c1}$ as shown in Fig. 76(b). Consequently, it is difficult to explain the expansion of the FEIC phase caused by the softening of the lowest spin-wave dispersion curve when we consider only a simple energy shift of the lowest excitation mode.

On the other hand, as we can see in Fig. 77, the doping of Ga$^{3+}$ ions gives a large effect on the ESR linewidth $\delta H_{ESR}$. Such ESR spectra suggest a broadening of the spin-wave excitation mode. This effect may cause the softening of the lower mode $\omega_L$. As shown in Fig. 76(b), by considering the broadening of the spin-wave excitation mode comparable to $\delta H_{ESR}$, we demonstrate the softening of the lowest excitation mode for the $x = 0.012$ sample.

Here, we discuss the change of the linewidth with the increase of $x$. We speculate that the ESR linewidth is highly correlated to the shift of $H_{c1}$, and thus we plot the linewidth $\delta H_{ESR}$ and the shift of $H_{c1}$ in the same figure as shown in Fig. 77. From the coincidence of these two values, we conclude that the dominant origin of the large shift of $H_{c1}$ is the ESR line broadening caused by doping of Ga$^{3+}$ ions.

Unusual broadening of the linewidth can not be explained simply by the randomness due to the substitution of nonmagnetic Ga$^{3+}$ ions for Fe$^{3+}$ ions. This result, however,
suggests that the substitution of nonmagnetic ions broadens the excitation branch unusually, and the softening of the lowest excitation branch by magnetic fields becomes easy. It was reported in a previous paper [113] that CuFeO₂ is a spin system coupled strongly with the lattice. We, thus, speculate that the randomness of the local lattice distortions caused by the nonmagnetic-ion doping makes the excitation mode broad. Consequently, we conclude that the expansion of the FEIC phase with the increase of $x$ is caused by broadening of the excitation branch, and probably induces the spin spiral correlation, resulting in ferroelectricity in the FEIC phase.

Next, we discuss magnetic transitions at $H_{c2}$, $H_{c3}$, $H_{c3'}$, $H_{c4}$ and $H_{c5}$ above $H_{c1}$. All these transition fields change slightly with increasing $x$ as shown in Fig. 68. The regions with collinear spin structures narrow slightly, and the collinear structures seem to be destabilized by Ga doping. In addition, a new magnetic phase 4th FI phase is observed between the 5SL and the 3SL phases. Although it is difficult to explain these results explicitly, we suggest following two possibilities as the origin of the change in the phase diagram.

The first possibility is a small reduction of the uniaxial anisotropy. The reduction of the $D$ value generally provides instability of collinear spin structures, and Fe³⁺ ions regain their original Heisenberg character. This is consistent with the theoretical finding on CuFeO₂ by Fishman et al. [63, 121]. In their $H$ versus $D/J_1$ phase diagram, the 3SL and the 5SL phases narrow with the reduction of $D$. This tendency is the same as that in our experiments. A field induced phase similar to the 4th FI phase was also observed in CuFeO₂⁺δ, and the oxygen nonstoichiometry makes the 20 T
transition split into two transitions at 20 T and 23 T \[122\], providing the possibility of the noncollinear three sublattice (NC-3i) phase that Fishman \textit{et al.} predicted. \[63\] In the phase diagram given by Fishman \textit{et al.}, the 5SL phase is next to the NC-3i phase, which may be realized by a weak change of magnetic anisotropy. The 4th FI phase observed from our magnetization measurements could be the NC-3i state in their phase diagram.

The second possibility is the alteration of spin-lattice coupling by Ga substitution. The substitution of Ga\textsuperscript{3+} ions, which differ in the ion radius from Fe\textsuperscript{3+}, affects the lattice state in CuFeO\textsubscript{2}. As already mentioned, recent theoretical studies pointed out that strong spin-lattice couplings favor a collinear magnetic state. In theoretical studies on CuFeO\textsubscript{2} by Wang \textit{et al.}, it is shown that the change of spin-lattice couplings brings about remarkably rich magnetic phases \[62\]. Therefore, we consider that the change of spin-lattice couplings in CuFeO\textsubscript{2} by the substitution of Ga\textsuperscript{3+} ions brings about a slight shift in the phase diagram, and realizes a new field-induced magnetic phase.

Finally, we discuss the biquadratic exchange interaction in CuFeO\textsubscript{2}. Lummen \textit{et al.} studied the successive field-induced phase transitions at low temperatures \[95\]. They considered that the biquadratic exchange interaction, the second and the third neighbor exchange interactions (\textit{J’},\textit{J”}), and trigonal anisotropy. The effective spin Hamiltonian for CuFeO\textsubscript{2} was constructed and given by,

\[
\mathcal{H} = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}(\mathbf{r}_i) \cdot \mathbf{S}(\mathbf{r}_j) + D(H)\sum_i (S^z(\mathbf{r}_i))^2 - \sum_{\langle ij \rangle} c(J_{ij} \mathbf{S}(\mathbf{r}_i) \cdot \mathbf{S}(\mathbf{r}_j))^2 - g_\text{\textsc{\textit{\textmu}}}B \sum_i S^z(\mathbf{r}_i) \cdot H,
\]

where \textit{c} is the biquadratic coupling constant, and \textit{D(H)} is the magnetic-anisotropy constant which is field dependent due to its strong coupling to the lattice distortion. The biquadratic term couples only nearest neighbor spin pairs (They ignore biquadratic term of second and third spin pairs for simplicity). Figures 78(a) and (b) show the calculated minimum energy per spin, and magnetization curve and easy-axis anisotropy.
respectively [95]. As shown in Fig. 78(a), their analysis seems to explain observed magnetic phase transitions below $H_{c5}$. The calculated magnetization curve is also in good agreement with the magnetization curve observed in previous experimental studies [94, 95] and our magnetization curve shown in Fig. 68. Therefore, we have analyzed ESR modes for the same model. The calculated result has a similar tendency to that obtained by our analysis without the biquadratic exchange interaction term (§ 4.4.5). Basically, a small biquadratic exchange interaction does not affect the lower ESR modes much. However, a difference of the energy dispersion between the models with and without the biquadratic exchange interaction term may occur. The calculation of the energy dispersion including the biquadratic exchange interaction term is quite difficult, and thus we omit it in this paper.

![Figure 78: (a) Calculated minimum energy per spin for each of the commensurate sublattice phases for $H||[001]$. (b) Field dependence ($H||[001]$) of the magnetization ($M$) and easy-axis anisotropy. The solid blue line shows a simulated magnetization process of CuFeO$_2$. The solid red line indicates the assumed value of the magnetic easy-axis anisotropy in the simulation of the various magnetic phases; $D$ is approximated to be proportional to $[M_{sat}-M(H)]$](image)

Macroscopical states in a frustrated system are quite sensitive to small perturbations or some parameters such as magnetic field, and thereby could inherently give rise to a number of different states. In particular, unusual magnetic phases are realized in CuFeO$_2$ in magnetic fields. The substitution of nonmagnetic Ga$^{3+}$ ions for Fe$^{3+}$ ions in CuFeO$_2$ changes the phase diagram and brings about interesting physical properties and rich magnetic phases.
4.7 Conclusions

We synthesized single crystals of the triangular-lattice antiferromagnet CuFe$_{1-x}$Ga$_x$O$_2$ with different $x$, and performed magnetization, electric polarization and multi-frequency ESR measurements on these single crystal samples. We observed a rapid expansion of the FEIC state by doping of Ga$^{3+}$ ions from magnetization and electric polarization measurements. The transition field $H_{cl}$ (4SL $\to$ FEIC) changes drastically by the doping.

Small change in the lowest ESR resonance mode and large broadening of the ESR line width were observed in the ESR measurements. It is suggested that magnetic phase transition from the 4SL (collinear four sublattice) to the FEIC (ferroelectric incommensurate) phases is not caused by the shift of the lowest excitation mode but by its large broadening. As a consequence, we conclude that the large shift of the transition field from the 4SL phase to the FEIC one is explained by the broadening of the excitation branch.

At higher magnetic field than $H_{cl}$, we observed a slight shift of the transition fields with increasing $x$ from the magnetization curves. We discuss two possibilities of the origin of this behavior, namely a small reduction of uniaxial anisotropy and an alternation of spin-lattice coupling by Ga substitution.
5 Summary

We summarize our studies on two types of two-dimensional frustrated antiferromagnets; KFe$_3$(OH)$_6$(SO$_4$)$_2$ and CuFe$_{1-x}$Ga$_x$O$_2$.

\[ S = \frac{5}{2} \text{ kagome lattice antiferromagnet } KFe$_3$(OH)$_6$(SO$_4$)$_2 \]
- Our experimental results (magnetization and ESR) are successfully explained by the same parameter set (exchange constants for intraplane and interplane, and the DM vectors).
- We conclude that the origin of anisotropy of this K-Fe-jarosite is the Dzyaloshinski-Moriya interaction, and the magnetization jump at 16 T is caused by the change of spin structure which arises from the competition between the DM interaction and the interplanar interaction.

\[ S = \frac{5}{2} \text{ triangular lattice antiferromagnet } CuFe$_{1-x}$Ga$_x$O$_2 \]
- It is suggested that magnetic phase transition from the 4SL to the FEIC phases is not caused by the shift of the excitation mode but by its broadening. As a result, we conclude that the large shift of the transition field from the 4SL phase into the FEIC one is explained by the broadening of the excitation branch.
- In the dispersion of spin wave excitation, minima appear at wave vectors associated with the incommensurate magnetic order. The softening of the minima must be a dynamic precursor to multiferroic phase. Therefore, the observation of spin wave excitation is helpful in research on multiferroic materials.
- We discuss two possibilities of the origin of slight shift of the transition fields at higher magnetic field with increasing \( x \), namely a small reduction of uniaxial anisotropy and an alternation of spin-lattice coupling by Ga substitution.

From these studies, we have found that the ground state natures of frustrated spin systems change drastically with a small perturbation, such as magnetic field and/or chemical doping. Our quantitative analyses by a mean-field approximation method on the experimental results of these classical two-dimensional frustrated antiferromagnets have clarified the details of spin dynamics in these compounds, and their magnetic properties are well explained.

The combination of high field magnetization and multi-frequency ESR results enables us to determine the physical parameters precisely. Moreover, pulsed strong magnetic fields enable us to approach interesting magnetic field-induced phases expected from spin frustration. As a consequence, we could discuss the behaviors of the frustrated magnets in magnetic fields in detail by utilizing these advantages.
Appendix I

In this appendix, I show the Mathematica program for the calculations of ESR resonance modes of the DM model for $H < H_c$. Other programs in §3 are too lengthy to show here, and thus omit them.

Clear[g, NA, uB, S, t, A, AI, J, Jmen, Dp, Dz, D12, D23, D31, D45, D56, D64, DD12, DD23, DD31, DD45, DD56, DD64, \[Theta]1, \[Theta]2, \[Theta]3, \[Theta]4, \[Theta]5, \[Theta]6, \[eta]1, \[eta]4, S1, S2, S3, S4, S5, S6, MM1x, MM2x, MM3x, MM4x, MM5x, MM6x, MM1y, MM2y, MM3y, MM4y, MM5y, MM6y, M1, M2, M3, M4, M5, M6, M1p, M2p, M3p, M4p, M5p, M6p, \[gamma], h, k, Ry, Rz, uhen, M1y, M2y, M3y, M4y, M5y, M6y, M1z, M2z, M3z, M4z, M5z, M6z, allmode, mode1, mode2, mode3, mode4, mode5, mode6, jika, energy, Fene, abc, bcd H1, H2, H3, H4, H5, H6, Hmax, dH]

(* Define parameters *)
k = 1.38066*10^{-23}; (* Boltzmann factor [J/K] *)
uB = 9.27408*10^{-24}; (* Bohr magneton [J/T] *)
NA = 6*10^{23}; (* Number of magnetic ions *)
h = 6.62617*10^{-34}; (* Planck constant [Js] *)
g = 2; (* g-factor *)
S = 5/2; (* Spin size *)

J = 42.3*k; (* Exchange interaction constant [K] *)
Jmen = -0.0966*k; (* Exchange interaction constant [K] *)
Dp = 1.62*k; (* DM component [K] *)
Dz = 1.97*k; (* DM component [K] *)
D12 = {-Sqrt[3]*Dp/2, -Dp/2, Dz}; (* DM vector *)
D23 = {0, Dp, Dz}; (* DM vector *)
D31 = {Sqrt[3]*Dp/2, -Dp/2, Dz}; (* DM vector *)
D45 = {-Sqrt[3]*Dp/2, -Dp/2, Dz}; (* DM vector *)
D56 = {0, Dp, Dz}; (* DM vector *)
D64 = {Sqrt[3]*Dp/2, -Dp/2, Dz}; (* DM vector *)

\[gamma] = 2 * Pi * g * uB / h; (* gyromagnetic ratio *)

A = 6 * 2 / NA * J / (g * uB)^2; (* For simplicity *)
A1 = 6 * 2 / NA * Jmen / (g * uB)^2; (* For simplicity *)
DD12 = 6 * 2 / NA * 2 * D12 / (g * uB)^2; (* For simplicity *)
DD23 = 6 * 2 / NA * 2 * D23 / (g * uB)^2; (* For simplicity *)
DD31 = 6 * 2 / NA * 2 * D31 / (g * uB)^2; (* For simplicity *)
DD45 = 6 * 2 / NA * 2 * D45 / (g * uB)^2; (* For simplicity *)
DD56 = 6 * 2 / NA * 2 * D56 / (g * uB)^2; (* For simplicity *)
DD64 = 6 * 2 / NA * 2 * D64 / (g * uB)^2; (* For simplicity *)
Hmax = 50; (* Maximum field for the calculation [T] *)
dH = 0.1; (* Interval field for the calculation [T] *)

θ1 = 3Pi/2;
θ2 = Pi/6;
θ3 = 5Pi/6;
θ4 = Pi/2;
θ5 = 7Pi/6;
θ6 = 11Pi/6;

\[ S1 = S \cdot \{ \cos(\theta_1) \cdot \cos(\eta_1), \sin(\theta_1) \cdot \cos(\eta_1), \sin(\eta_1) \} \]
\[ S2 = S \cdot \{ \cos(\theta_2) \cdot \cos(\eta_1), \sin(\theta_2) \cdot \cos(\eta_1), \sin(\eta_1) \} \]
\[ S3 = S \cdot \{ \cos(\theta_3) \cdot \cos(\eta_1), \sin(\theta_3) \cdot \cos(\eta_1), \sin(\eta_1) \} \]
\[ S4 = S \cdot \{ \cos(\theta_4) \cdot \cos(\eta_4), \sin(\theta_4) \cdot \cos(\eta_4), \sin(\eta_4) \} \]
\[ S5 = S \cdot \{ \cos(\theta_5) \cdot \cos(\eta_4), \sin(\theta_5) \cdot \cos(\eta_4), \sin(\eta_4) \} \]
\[ S6 = S \cdot \{ \cos(\theta_6) \cdot \cos(\eta_4), \sin(\theta_6) \cdot \cos(\eta_4), \sin(\eta_4) \} \]

(* Calculate magnetization from 0 T to Hmax T every dH T and output
results in "henka={ field, energy,η1, η4, jika } ") *

henka = Table[H,

Clear[η1, η4, M3x, M1y, M2y, M3y];

- g*u*B*(S1[[3]] + S2[[3]] + S3[[3]] + S4[[3]] + S5[[3]] + S6[[3]]);

abc = FindMinimum[energy * 10^50, {η1, 0}, {η4, 0}];
energy,

η1 = (η1 /. Last[abc]);
η4 = (η4 /. Last[abc]);
(g * S * Sin[η1] + g * S * Sin[η4]) / 2

, {H, 0, Hmax, dH}];

jika = Table[{henka[[x, 1]], henka[[x, 5]]}, {x, 1, Hmax/dH + 1}];

Export["jika.txt", jika, "Table"];

M1 = {MM1x, MM1y, MM1z};
M2 = {MM2x, MM2y, MM2z};
M3 = {MM3x, MM3y, MM3z};
M4 = {MM4x, MM4y, MM4z};
\[ M_5 = \{M_{5x}, M_{5y}, M_{5z}\}; \]
\[ M_6 = \{M_{6x}, M_{6y}, M_{6z}\}; \]

\[
\text{Fene} = DD12.\text{Cross}[M_1, M_2] + DD23.\text{Cross}[M_2, M_3] + DD31.\text{Cross}[M_3, M_1] +
\sin{(M_1.M_5 + M_1.M_6 + M_2.M_6 + M_2.M_4 + M_3.M_5 + M_3.M_4)} -
\]
\[
\text{H}_1 = \{-D[\text{Fene}, M_{1x}], -D[\text{Fene}, M_{1y}], -D[\text{Fene}, M_{1z}]\}
\]
\[
\text{H}_2 = \{-D[\text{Fene}, M_{2x}], -D[\text{Fene}, M_{2y}], -D[\text{Fene}, M_{2z}]\}
\]
\[
\text{H}_3 = \{-D[\text{Fene}, M_{3x}], -D[\text{Fene}, M_{3y}], -D[\text{Fene}, M_{3z}]\}
\]
\[
\text{H}_4 = \{-D[\text{Fene}, M_{4x}], -D[\text{Fene}, M_{4y}], -D[\text{Fene}, M_{4z}]\}
\]
\[
\text{H}_5 = \{-D[\text{Fene}, M_{5x}], -D[\text{Fene}, M_{5y}], -D[\text{Fene}, M_{5z}]\}
\]
\[
\text{H}_6 = \{-D[\text{Fene}, M_{6x}], -D[\text{Fene}, M_{6y}], -D[\text{Fene}, M_{6z}]\}
\]

(* The motion of each sublattice moment *)
\[
\text{M}_{1p} = \{\text{NA}^*g^*uB^*/6, M_{1y}^*\exp[i*\omega *t], M_{1z}^*\exp[i*\omega *t] \};
\]
\[
\text{M}_{2p} = \{\text{NA}^*g^*uB^*/6, M_{2y}^*\exp[i*\omega *t], M_{2z}^*\exp[i*\omega *t] \};
\]
\[
\text{M}_{3p} = \{\text{NA}^*g^*uB^*/6, M_{3y}^*\exp[i*\omega *t], M_{3z}^*\exp[i*\omega *t] \};
\]
\[
\text{M}_{4p} = \{\text{NA}^*g^*uB^*/6, M_{4y}^*\exp[i*\omega *t], M_{4z}^*\exp[i*\omega *t] \};
\]
\[
\text{M}_{5p} = \{\text{NA}^*g^*uB^*/6, M_{5y}^*\exp[i*\omega *t], M_{5z}^*\exp[i*\omega *t] \};
\]
\[
\text{M}_{6p} = \{\text{NA}^*g^*uB^*/6, M_{6y}^*\exp[i*\omega *t], M_{6z}^*\exp[i*\omega *t] \};
\]

(* Transform matrix *)
\[
\text{R}_{y}[y] := \{\cos[y], \sin[y], 0\}, \{-\sin[y], \cos[y]\}, 0\}, \{0, 1, 0\};
\]
\[
\text{R}_{z}[z] := \{\cos[z], 0, -\sin[z]\}, \{0, 1, 0\}, \{\sin[z], 0, \cos[z]\};
\]

(* Calculate magnetization from 0 T to "Hmax" T every "dH" T and output results in "allmode={field, model1, model2, model3, mode4, mode5, mode6}" *)
\[
\text{allmode} = \text{Table}[(\{\text{ab}/10 - 0.1,}
\]
\[
\text{Clear}[M_{1y}, M_{2y}, M_{3y}, M_{4y}, M_{5y}, M_{6y}, M_{1z}, M_{2z}, M_{3z}, M_{4z}, M_{5z}, M_{6z}];
\]

(* Transform the new coordinate system assumed on each sublattice moment into the initial one *)
\[
\text{M}1 = \text{R}_{y}[\theta_1].\text{M}_{1p};
\]
\[
\text{M}2 = \text{R}_{y}[\theta_2].\text{M}_{2p};
\]
\[
\text{M}3 = \text{R}_{y}[\theta_3].\text{M}_{3p};
\]
\[
\text{M}4 = \text{R}_{y}[\theta_4].\text{M}_{4p};
\]
\[
\text{M}5 = \text{R}_{y}[\theta_5].\text{M}_{5p};
\]
\[
\text{M}6 = \text{R}_{y}[\theta_6].\text{M}_{6p};
\]
\[
\text{M}_{1x} = \text{M}1[[1]]; \text{M}_{1y} = \text{M}1[[2]]; \text{M}_{1z} = \text{M}1[[3]];
MM2x = M2[[1]]; MM2y = M2[[2]]; MM2z = M2[[3]];  
MM3x = M3[[1]]; MM3y = M3[[2]]; MM3z = M3[[3]];  
MM4x = M4[[1]]; MM4y = M4[[2]]; MM4z = M4[[3]];  
MM5x = M5[[1]]; MM5y = M5[[2]]; MM5z = M5[[3]];  
MM6x = M6[[1]]; MM6y = M6[[2]]; MM6z = M6[[3]];  

\[ t = 0; \]

(* Solve the equation of motion \( \frac{dM}{dt} = M \times H \) *)

(* The right side of the equation of motions *)

\[
\text{uhen} = \{ \text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M1y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M2y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M3y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M4y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M5y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M6y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M1z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M2z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M3z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M4z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M5z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[01]].Cross[M1,H1].{0,1,0},M6z] } \};
\]

\[
\{ \text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M1y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M2y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M3y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M4y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M5y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M6y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M1z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M2z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M3z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M4z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M5z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[02]].Cross[M2,H2].{0,1,0},M6z] } \};
\]

\[
\{ \text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M1y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M2y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M3y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M4y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M5y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M6y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M1z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M2z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M3z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M4z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M5z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[03]].Cross[M3,H3].{0,1,0},M6z] } \};
\]

\[
\{ \text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M1y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M2y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M3y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M4y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M5y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M6y],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M1z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M2z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M3z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M4z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M5z],} \\
\text{D[Inverse[Rz[henka[ab,3]]].Inverse[Ry[04]].Cross[M4,H4].{0,1,0},M6z] } \};
\]

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\[
\{ D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_2,H_2], \{0,0,1\}, M_{1y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_2,H_2], \{0,0,1\}, M_{2y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_2,H_2], \{0,0,1\}, M_{3y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_2,H_2], \{0,0,1\}, M_{4y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_2,H_2], \{0,0,1\}, M_{5y} \}, \\
\} \\
\{ D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_2,H_2], \{0,0,1\}, M_{6y} \} , \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_3,H_3], \{0,0,1\}, M_{1y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_3,H_3], \{0,0,1\}, M_{2y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_3,H_3], \{0,0,1\}, M_{3y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_3,H_3], \{0,0,1\}, M_{4y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_3,H_3], \{0,0,1\}, M_{5y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_3,H_3], \{0,0,1\}, M_{6y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_4,H_4], \{0,0,1\}, M_{1y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_4,H_4], \{0,0,1\}, M_{2y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_4,H_4], \{0,0,1\}, M_{3y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_4,H_4], \{0,0,1\}, M_{4y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_4,H_4], \{0,0,1\}, M_{5y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_4,H_4], \{0,0,1\}, M_{6y} \}, \\
\} \\
\{ D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{1y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{2y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{3y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{4y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{5y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{6y} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{1z} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{2z} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{3z} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{4z} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{5z} \}, \\
D^{-1}[Rz[\text{Henka}[ab,4]]], D^{-1}[Ry[\theta]], \text{Cross}[M_5,H_5], \{0,0,1\}, M_{6z} \} 
\]
\( D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta5]].\text{Cross}[M5,H5].\{0,0,1\},M6z] \) ,
\{ D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M1y],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M2y],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M3y],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M4y],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M5y],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M6y],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M1z],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M2z],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M3z],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M4z],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M5z],
D[\text{Inverse}[Rz[\text{henka}[[ab,4]]]].\text{Inverse}[Ry[\theta6]].\text{Cross}[M6,H6].\{0,0,1\},M6z] \} }

\( M1y = 0; \) \( M2y = 0; \) \( M3y = 0; \) \( M4y = 0; \) \( M5y = 0; \) \( M6y = 0; \)
\( M1z = 0; \) \( M2z = 0; \) \( M3z = 0; \) \( M4z = 0; \) \( M5z = 0; \) \( M6z = 0; \)

\( (*) \) \text{Solve an eigenvalue problem of the "uhen" *)}
\( bcd = \text{Re[Eigensystem[uhen/((ih)/(2\gamma uB))/2/Pi/10^9]}; \)
\( \text{koyuchi} = \text{bcd}[1]; \)
\( \text{Abs[koyuchi}[2]], \text{Abs[koyuchi}[4]], \text{Abs[koyuchi}[6]]] \}
\( \text{Abs[koyuchi}[8]], \text{Abs[koyuchi}[10]], \text{Abs[koyuchi}[12]]] \}

\( * \) \text{Assign the obtained three eigenvalues to three resonance modes *}
\( \text{mode1} = \text{Table[allmode}[x, 1], \text{allmode}[x, 2]], \{x, 1, \text{Hmax/dH} + 1\}; \)
\( \text{mode2} = \text{Table[allmode}[x, 1], \text{allmode}[x, 3]], \{x, 1, \text{Hmax/dH} + 1\}; \)
\( \text{mode3} = \text{Table[allmode}[x, 1], \text{allmode}[x, 4]], \{x, 1, \text{Hmax/dH} + 1\}; \)
\( \text{mode4} = \text{Table[allmode}[x, 1], \text{allmode}[x, 5]], \{x, 1, \text{Hmax/dH} + 1\}; \)
\( \text{mode5} = \text{Table[allmode}[x, 1], \text{allmode}[x, 6]], \{x, 1, \text{Hmax/dH} + 1\}; \)
\( \text{mode6} = \text{Table[allmode}[x, 1], \text{allmode}[x, 7]], \{x, 1, \text{Hmax/dH} + 1\}; \)

\( (*) \) \text{Out put as txt files *)}
\( \text{Export["mode1.txt", mode1, "Table"]}; \)
\( \text{Export["mode2.txt", mode2, "Table"]}; \)
\( \text{Export["mode3.txt", mode3, "Table"]}; \)
\( \text{Export["mode4.txt", mode4, "Table"]}; \)
\( \text{Export["mode5.txt", mode5, "Table"]}; \)
\( \text{Export["mode6.txt", mode6, "Table"]}; \)
Appendix II

In this appendix, I show the Mathematica program for the calculations of energy dispersion curves in the 4 sub-lattice phase. Other programs in § 4 are too lengthy to show here, and thus omit them.

Clear[m, J1, J2, J3, Jz, JII, JIII, D1, H, S, P, Q, kx, ky, kz,
Ak, Bk, Ck, Dk, Fk, A2k, Ck2, Dk2, Dk2d, x, dk, hmin, hmax, s,
egA, egB, egA2, egA3, egA4, s1, s2, s3, s4, mat1, h,
Int1, Int2, Int3, In1, In3, sd1, sd2, sd3, sd4, Intd1, Intd2, Intd3, Ind1, Ind3]

mode = Table[
{x, (* Define parameters *)
  dk = 0.01; hmin = 0; hmax = 0.5;
  J1 = 3.0*20.8357/241.9;
  J2 = 3.4*20.8357/241.9;
  J3 = 2.0*20.8357/241.9;
  Jz = 0.59*20.8357/241.9;
  JII = 1.1*20.8357/241.9;
  JIII = 2.2*20.8357/241.9;
  D1 = -0.33*20.8357/241.9;
  El = 0.07*20.8357/241.9;
  H = 0*7.26*27.992/241.9;
  S = 5/2;
  Akx = -2*S*(J1 + J2 - J3 + Jz - D1 - El);
  Aky = -2*S*(J1 + J2 - J3 + Jz - D1 + El);
  Ck = -2*S*J1*Cos[kx + ky] - 2*S*Jz*Cos[kz];
  Dk = -S*J3*(Exp[I*kx] + Exp[I*ky]) -
      S*Jz*(Exp[I*(-kx/3 - 2*ky/3 + kz)] + Exp[I*(-2*kx/3 - ky/3 - kz)]);
  Bk = -S*J2*(Exp[-I*kx] + Exp[-I*ky]) -
      S*Jz*(Exp[I*(kx/3 + 2*ky/3 + kz)] + Exp[I*(2*kx/3 + ky/3 - kz)]);
  Ek = -S*J3*(Exp[-I*kx] + Exp[-I*ky]) -
      S*Jz*(Exp[I*(kx/3 + 2*ky/3 + kz)] + Exp[I*(2*kx/3 + ky/3 - kz)]);
  Fk = -S*J2*(Exp[I*kx] + Exp[I*ky]) -
      S*Jz*(Exp[I*(-kx/3 - 2*ky/3 + kz)] + Exp[I*(-2*kx/3 - ky/3 - kz)]);
  Ak2 = 2*S*(JII*(1 - Cos[-kx + ky]) - JIII*(1 + Cos[2*(kx + ky)]));
  Ck2 = -2*S*(JII*(Cos[2*kx] + Cos[2*ky]));
  Dk2 = -S*JII*(Exp[(-1)*I*(2*kx + ky)] + Exp[(-1)*I*(kx + 2*ky)]);
  Dk2d = Conjugate[Dk2];

kx = ky = x*2*Pi;
\text{kz} = \pi;

\text{m} = \{0, -(Ax + Ak_2) + H, 0, -(Cx + Ck_2), 0, -(Dk + Dk_2), 0, -(Bk + Dk_2d)}

\{(Ax + Ak_2) - H, 0, (Cx + Ck_2), 0, (Dk + Dk_2), 0, (Bk + Dk_2d), 0\},

\{0, Ck + Ck_2, 0, Ax + Ak_2 + H, 0, Bk + Dk_2d, 0, Dk + Dk_2\},

\{-Ck - Ck_2, 0, -Ax - Ak_2 - H, 0, -Bk - Dk_2d, 0, -Dk - Dk_2, 0\},

\{0, -(Ek + Dk_2d), 0, -(Fk + Dk_2), 0, -(Ax + Ak_2) + H, 0, -(Cx + Ck_2)\},

\{Ek + Dk_2d, 0, Fk + Dk_2, 0, Ak + Ak_2 - H, 0, Ck + Ck_2, 0 \},

\{0, Fk + Dk_2, 0, Ek + Dk_2d, 0, Ck + Ck_2, 0, Ax + Ak_2 + H \},

\{-Fk - Dk_2, 0, -Ek - Dk_2d, 0, -Ck - Ck_2, 0, -Ax - Ak_2 - H, 0 \}\};

Q = \text{Abs}\{\text{Eigenvalues}[m]\};

\text{Abs}[Q[[1]]], \text{Abs}[Q[[3]]], \text{Abs}[Q[[5]]], \text{Abs}[Q[[7]]]\}

, \{x, 0, 0.5, 0.001\};

\text{mode1} = \text{Table}[\text{mode}[y, 1], \text{mode}[y, 2], y, 1, 501];
\text{mode2} = \text{Table}[\text{mode}[y, 1], \text{mode}[y, 3], y, 1, 501];
\text{mode3} = \text{Table}[\text{mode}[y, 1], \text{mode}[y, 4], y, 1, 501];
\text{mode4} = \text{Table}[\text{mode}[y, 1], \text{mode}[y, 5], y, 1, 501];

\text{Export["mode1.txt", mode1, "Table"]}
\text{Export["mode2.txt", mode2, "Table"]}
\text{Export["mode3.txt", mode3, "Table"]}
\text{Export["mode4.txt", mode4, "Table"]}
References


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Publication List

1. “New high magnetic field phase of the frustrated $S = 1/2$ ferromagnetic chain LiCuVO$_4$”

2. “Multi-frequency ESR in the $S = 5/2$ triangular-lattice antiferromagnet CuFe$_{1-x}$Ga$_x$O$_2$ ”

3. “Possibility of the field-induced spin-nematic phase in LiCuVO$_4$”

4. “Multifrequency ESR measurements of the triangular lattice antiferromagnet CuFeO$_2$ in high magnetic fields ”

5. “Electromagnon excitation in the triangular lattice antiferromagnet CuFeO$_2$ ”

6. “High-field multi-frequency ESR in the $S = 5/2$ kagome-lattice antiferromagnet KFe$_3$(OH)$_6$(SO$_4$)$_2$ ”

7. “ $S = 5/2$ カゴメ格子ハイゼンベルグ反強磁性体 KFe$_3$(OH)$_6$(SO$_4$)$_2$ の強磁場多周波 ESR”
   T. Fujita, M. Hagiwara

8. “ Multi-frequency ESR in the $S = 1/2$ frustrated chain compound LiCuVO$_4$ ”

9. “Electromagnon Excitation of the Triangular Lattice Antiferromagnet CuFeO$_2$ in High Magnetic Field”
   S. Kimura, K. Watanabe, T. Fujita, M. Hagiwara, H. Yamaguchi, T. Kashiwagi,
N. Terada.

10. “High-field magnetism of the $S = 5/2$ kagome-lattice antiferromagnet KFe$_3$(OH)$_6$(SO$_4$)$_2$
for the magnetic field in the kagome-plane”

11. ” Antiferromagnetic resonance in One-dimensional magnet IPACu(Chi-xBrx)$_3$
$(x=0.83) ”
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Journal of Korean Physical Society, in press.

12. “High field magnetism of the $S = 5/2$ triangular-lattice antiferromagnet CuFe$_{1-x}$Ga$_x$O$_2$
$(x=0 \sim 0.028)”
submitted to Journal of the Physical Society of Japan.

13. “Evidence for magnetic Rh$^{3+}$ in the layered rhodium oxide LaSrRhO$_4$ ”
submitted to Physical Review B.

14. “Incommensurate correlations in Cs$_2$CuBr$_4$ in the disordered phase”
submitted to Physical Review B.

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