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

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Abstract. We have performed multi-frequency electron spin resonance (ESR) and magnetization measurements on single crystals of the triangular-lattice antiferromagnet CuFe$_{1-x}$Ga$_x$O$_2$ ($x=0.000-0.028$) to clarify the origin of the shift of the magnetic transition field from an Ising-like four-sublattice phase into an incommensurate phase by doping of Ga$^{3+}$. As a result, we have succeeded in explaining the shift of transition field by broadening of the lowest excitation branch.

1. Introduction

Frustrated spin systems provide a rich variety of magnetic states, such as spin liquid [1], spin nematic [2], and spin ice [3]. In particular, magnetic substances with ferroelectricity induced by the spiral magnetic structure due to frustration have drawn attention to condensed matter scientists and engineers as multiferroic materials in recent years [4].

A delafosite compound CuFeO$_2$ is an extensively-studied triangular-lattice magnet [5]. Triangular-lattice antiferromagnets have attracted considerable interest as one of the most typical frustrated spin systems. CuFeO$_2$ consists of triangular layers of Fe$^{3+}$ ($3d^5$) ions which are separated by nonmagnetic layers of Cu$^+$ and O$^2-$ ions and are stacked perpendicularly to the $c$-axis. Since Fe$^{3+}$ ions with $3d^5$ high-spin configuration have no orbital angular momentum, this is usually regarded as a Heisenberg-type spin system. However, CuFeO$_2$ exhibits an Ising-like four-sublattice (4SL) ($\uparrow\uparrow\downarrow\downarrow$) collinear order below 11 K at zero magnetic field. Moreover, the several successive phase transitions take place well below 11 K, when the external field $H$ along the $c$-axis is increased. Above $H_c = 7$ T, ferroelectric and incommensurate (FEIC) order (7 T $< H < 13$ T) is realized, and then a five-sublattice (5SL) ($\uparrow\uparrow\uparrow\downarrow\downarrow$), a three-sublattice (3SL) ($\uparrow\uparrow\downarrow$), and a one-sublattice (1SL) ($\uparrow\uparrow\downarrow$) orders are observed [6].

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 $H_c$ with increasing the concentration of nonmagnetic ions. As a result, the FEIC phase can be induced at zero magnetic field by a certain amount of nonmagnetic ions [7]. This result indicates that the ferroelectric phase becomes stable and the realization of this phase can be controlled by substitution of nonmagnetic ions.

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ESR is one of the powerful tools to investigate magnetic excitations with high resolution. We have performed multi-frequency ESR measurements to clarify why the transition field \( H_c \) goes down with increasing \( x \) in \( \text{CuFe}_{1-x}\text{Ga}_x\text{O}_2 \) from the viewpoint of magnetic excitations.

2. Experimental

In this study, we synthesized some single crystal samples of \( \text{CuFe}_{1-x}\text{Ga}_x\text{O}_2 \) with different Ga contents. The single crystals with different \( x \) (\( x = 0.000, 0.001, 0.008, 0.012, 0.013, \) and 0.028) were grown by a floating zone (FZ) technique \([8]\). We verified that the samples are in a single phase by powder X-ray diffraction. We also determined the crystal axes and Ga contents by Laue photography and inductively-coupled plasma mass spectrometer (ICP-MS), respectively. We performed ESR measurements at frequencies below 500 GHz in static magnetic fields of up to 8 T at 1.6 K by utilizing a 16 T superconducting magnet (Oxford Instruments) and a vector network analyzer (AB millimetre). High-field magnetization measurements were performed in pulsed magnetic fields of up to 20 T. The magnetization was measured with an induction method using a pick-up coil. The magnetization at 4.2 K in magnetic fields of up to 7 T was also measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL7). All the experiments were carried out at KYOKUGEN in Osaka University.

3. Experimental Results

Figures 1 (a) and (b) show magnetization curves at 4.2 K for \( H//c \) of \( \text{CuFe}_{1-x}\text{Ga}_x\text{O}_2 \) with \( x = 0.000 \) and 0.028, respectively. In the magnetization curve for \( x = 0.000 \), steep increases, which correspond to the magnetic transitions reported previously, appear at about 7 T and 13 T. Large hysteresis observed in the curve indicates that the first order transitions occur at these fields. The field region between 7 T and 13 T is reported to be a FEIC phase. In Fig. 1 (b), we observed only one transition corresponding to higher transition in Fig. 1 (a), and thus the systematic shift of the FEIC state occurs by doping. It is depicted in Fig. 2 magnetic field \((H)\) versus Ga\(^{3+}\) content \((x)\) phase diagram determined by the magnetization measurements at 4.2 K and 1.3 K.

![Figure 1](image1.png)

**Figure 1.** (a) Magnetization curves of \( \text{CuFe}_{1-x}\text{Ga}_x\text{O}_2 \) with \( x = 0.000 \) at 4.2 K for \( H//c \). The steps at about 7 T and 13 T correspond to the transitions from a four-sublattice (4SL) to a ferroelectric incommensurate (FEIC) phase and from the FEIC to a five-sublattice (5SL) phase, respectively. (b) Magnetization curves of \( \text{CuFe}_{1-x}\text{Ga}_x\text{O}_2 \) with \( x = 0.028 \) at 4.2 K for \( H//c \). The step at 10 T corresponds to the transition from the FEIC to the 5SL phase.
This result suggests that ferroelectric phase becomes stable with the substitution of nonmagnetic ions for Fe$^{3+}$ ions.

We observed some ESR signals in CuFe$_{1-x}$Ga$_x$O$_2$ ($x$ less than 0.012) and the resonance fields for $x = 0.000$ and 0.012 are plotted on the frequency-field plane as shown in Fig. 3. The resonance branches for $x = 0.012$ slightly shift to the low frequency side compared with those for $x = 0.000$. The resonance mode at zero field changes only about 15 GHz. On the contrary, the linewidth changes dramatically with the increase of $x$ in CuFe$_{1-x}$Ga$_x$O$_2$ as shown in Fig. 4. The linewidth broadens with increasing $x$. The full widths at half maximum for $x = 0.000$ and $x = 0.012$ are about 0.2 T and 1.3 T, respectively.

![Figure 2. Phase diagram of magnetic field $H$ versus Ga content $x$. Black circles show the transition field from the 4SL to the FEIC phase determined by the ascending magnetization process. Black squares show the transition field from the FEIC to the 5SL phase determined by the ascending magnetization process. As compared with the transition field from the FEIC to the 5SL phase, the transition field from the 4SL to the FEIC phase shifts rapidly with the increase of Ga$^{3+}$ content.](image1)

![Figure 3. Frequency-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 $H//c$. Closed and open circles denote the ESR resonance points observed in CuFe$_{1-x}$Ga$_x$O$_2$ for $x = 0.000$ and 0.012, respectively. We found a small shift of the excitation mode by Ga doping.](image2)
4. Discussion

The transition from the 4SL state to the FEIC one is understood as the softening of magnetic excitation mode [9]. As we can see in the previous section, Ga$^{3+}$ doping gives a large effect on the excitation mode. First, we consider the shift of the lowest excitation mode. It seems too small to explain the large shift of $H_c$, which is defined by the change of the transition field from the $x=0.000$ value in the field-ascending process of magnetization curve, and thus the shift of the excitation mode of only 15 GHz (the order of 0.1 T) is thought to be no origin of the large shift of $H_c$. Next, we consider the change of linewidth with the increase of $x$. The ESR linewidths are highly correlated to the shifts of $H_c$ as shown in Fig. 5. Accordingly, we conclude that the dominant origin of the large shift of $H_c$ is the ESR line broadening caused by doping of nonmagnetic ions.

Unusual broadening of the linewidth can not be explained simply by the randomness due to the substitution of nonmagnetic ions for Fe$^{3+}$. This result, however, suggests that the substitution of nonmagnetic ions makes the excitation branch broad, and the softening of the lowest excitation branch by magnetic fields becomes easier. It was reported in a previous study [10] that CuFeO$_2$ has 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 stabilization of the FEIC phase with the increase of $x$ is caused by broadening of the excitation branch which probably induces the spin spiral correlation, resulting in ferroelectricity in the FEIC phase. Quite recently, inelastic neutron scattering (INS) measurements on a single crystal sample with $x=0.035$ which is larger than the $x$ in our samples [11] were carried out and it was
reported that the FEIC state is realized by softening of the excitation branch. This statement is not contradictory to our experimental results because of the experimental resolution. In our ESR measurements, the energy resolution is less than the order of $10^{-3}$ meV, while the resolution of INS measurements using cold neutron beam is at least $10^{-1}$ meV as you can see in Fig. 2(a) or Fig. 3(a) in Ref. [11]. Therefore, an INS measurement is not really suitable for investigating extremely low energy properties of condensed matters. Besides, the INS measurements were done on the 3.5 % Ga content sample which is in the FEIC phase at zero magnetic field and no phase transition in a magnetic field was observed in such a high Ga content sample.

5. Conclusion
We synthesized single crystals of the triangular-lattice antiferromagnet CuFe$_{1-x}$Ga$_x$O$_2$ with different $x$, and have performed multi-frequency ESR and magnetization measurements. Small changes in the ESR resonance modes and large broadening of the ESR spectra were observed from the ESR measurements. 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.

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