Magnetic ordering and fluctuation in kagomé lattice antiferromagnets, Fe and Cr jarosites

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Abstract

Jarosite family compounds, $\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$, (abbreviate Fe jarosite), and $\text{KCr}_3(\text{OH})_6(\text{SO}_4)_2$, (Cr jarosite), are typical examples of the Heisenberg antiferromagnet on the kagomé lattice and have been investigated by means of magnetization and NMR experiments. The susceptibility of Cr jarosite deviates from Curie-Weiss law due to the short-range spin correlation below about 150 K and shows the magnetic transition at 4.2 K, while Fe jarosite has the transition at 65 K. The susceptibility data fit well with the calculated one on the high temperature expansion for the Heisenberg antiferromagnet on the kagomé lattice. The values of exchange interaction of Cr jarosite and Fe jarosite are derived to be $J_{\text{Cr}} = 4.9$ K and $J_{\text{Fe}} = 23$ K, respectively. The $^1\text{H}$-NMR spectra of Fe jarosite suggest that the ordered spin structure is the $\mathbf{q} = 0$ type with positive chirality of the 120° configuration. The transition is caused by a weak single-ion type anisotropy. The spin-lattice relaxation rate, $1/T_1$, of Fe jarosite in the ordered phase decreases sharply with lowering the temperature and can be well explained by the two-magnon process of spin wave with the anisotropy.
I. INTRODUCTION

The antiferromagnets on the kagomé lattice have frustration due to the competition of the antiferromagnetic interactions between neighboring spins. The antiferromagnets on the triangular lattice also have been well known as the frustration systems. While the triangular lattice has 6 nearest neighbors and the adjacent triangles on the triangular lattice share one side, or 2 lattice points, in common, the kagomé lattice has only 4 nearest neighbors and the adjacent triangles on the kagomé lattice share only one lattice point in common. Thus the spins on the kagomé lattice suffer smaller restriction from neighboring spins than the spins on the triangular lattice. The Heisenberg antiferromagnet on the kagomé lattice exhibits infinite and continuous degeneracy of the ground state. Theoretically the two-dimensional isotropic Heisenberg kagomé lattice antiferromagnet have no magnetic phase transition at finite temperature. The thermal or the quantum fluctuation, however, resolves the degeneracy of the ground state [1,2]. This effect induces the coplanar spin arrangement and two Néel states have been discussed as candidates for the spin structure at zero temperature. One is a $q = 0$ type and the other is a $\sqrt{3} \times \sqrt{3}$ type of the 120° structure. Theoretical studies suggest that the latter is favored slightly [1]. When a weak Ising-like anisotropy is introduced into the Hisenberg kagomé lattice antiferromagnet, the system has the magnetic phase transition at finite temperature and has a peculiar spin structure [3]. Small perturbation, anisotropy or distortion may resolve the degeneracy of frustrated systems and cause the phase transition.

The jarosite family compounds, KCr$_3$(OH)$_6$(SO$_4$)$_2$ and KFe$_3$(OH)$_6$(SO$_4$)$_2$ are examples of the Heisenberg kagomé lattice antiferromagnets [4,5]. We have investigated these powder samples by the measurements of magnetization and the $^1$H nuclear magnetic resonance experiments to clarify the magnetic transition and the spin fluctuation in the Heisenberg kagomé lattice antiferromagnet [6]. The magnetic ions Cr$^{3+}$ and Fe$^{3+}$ have spins 3/2 and 5/2, respectively. The ions form the kagomé lattice on the $c$-plane and interact antiferromagnetically with each other. The protons observed by NMR locate nearly on the kagomé
planes. Adjacent kagomé planes are separated by nonmagnetic ions, S, O, H and K with the long interaction paths, so that the interplane magnetic interaction is very weak.

II. EXPERIMENTAL RESULTS

The magnetization was measured using a SQUID magnetometer in the temperature range between 2 K and 300 K. Figures 1 and 2 show the susceptibility of Fe jarosite and Cr jarosite, respectively. The susceptibility of Fe jarosite has the cusp at $T_{N[Fe]} = 65$ K, while the susceptibility of Cr jarosite increases abruptly below 4.2 K.

The susceptibility for the Heisenberg kagomé lattice antiferromagnet has been calculated by the high temperature expansion up to the 8th order and the result is extended to the lower temperature by the Padé [4,4] approximants \cite{7}. Figure 3 shows the comparison between the experimental and theoretical inverse susceptibility for Cr jarosite. The experimental values deviate clearly from the Curie-Weiss law below about 150 K and fit very well with the calculated curves above 20 K. The values of the exchange interaction for Cr jarosite and Fe jarosite are derived to be $J_{Cr}/k_B = 4.9$ K and $J_{Fe}/k_B = 23$ K, respectively. The theoretical susceptibility deviates remarkably from Curie-Weiss law below about $8JS(S+1)/k_B$ due to the development of short-range spin correlation. For Fe jarosite the value of $8JS(S+1)/k_B$ is about 1600 K, that is far away from the experimental temperature region. For the other kagomé lattice antiferromagnet SrCr$_{8-x}$Ga$_{4+x}$O$_{19}$ the value is about 860 K and is also large \cite{7,8}. The value for Cr jarosite is about 150 K, that is in the experimental temperature region. Thus Cr jarosite is a good example to show the deviation from the Curie-Weiss law owing to the small $J$ and $S$ values.

The $^1$H-NMR spectrum of Fe jarosite has a sharp peak in the paramagnetic phase, while the spectrum below 65 K becomes to be broader and shows typical pattern for the powder antiferromagnets \cite{9}. This transition temperature coincides with the susceptibility data and the spectrum indicates the antiferromagnetic ordering.

The spin-lattice relaxation rates, $1/T_1$, of $^1$H in Fe jarosite is shown in Fig. 4. The rate
1/$T_1$ in the paramagnetic phase slightly increases as temperature approaches to $T_{N[Fe]}$. The rate in the ordered phase decreases sharply as temperature is lowered.

The NMR spectrum for Cr jarosite has a sharp peak in the paramagnetic phase, while the half width increases below 4.2 K. The rate 1/$T_1$ for Cr jarosite is almost independent of the temperature in paramagnetic phase, however, it decreases below 4.2 K as temperature is lowered.

**III. DISCUSSION**

The NMR spectrum of Fe jarosite indicates that all protons feel same magnitude of internal dipolar field from Fe$^{3+}$ spins. This suggests that the ordered spin structure is the $q = 0$ type of the 120° configuration with positive chirality. If there existed the magnetic alignment with negative chirality, two kinds of proton sites with different magnitude of the internal field must exist. The neutron diffraction experiments confirmed this magnetic structure and revealed that the spins direct to or from the center of triangle on the kagomé lattice [11].

This spin structure is considered to be caused by the single-ion type anisotropy of magnetic ions. Each magnetic ion is surrounded by an octahedron composed of six oxygens, whose principal axis cants about $\theta = 20^\circ$ from the $c$-axis towards the center of a triangle and the octahedron deforms slightly. The deformation and the canting of the octahedron must cause the single-ion anisotropy. The spin system can be expressed as,

$$\mathcal{H} = 2J \sum_{<i,j>} \mathbf{S}_i \cdot \mathbf{S}_j + D \sum_i (S^z_i)^2 - E \sum_i \{(S^x_i)^2 - (S^y_i)^2\},$$  \hspace{1cm} (1)

where the local coordinate ($x', y', z'$) for each ion is determined by the relation with each surrounding octahedron, $D > 0$ and $E > 0$. In the case of

$$E > D \frac{\sin^2 \theta}{1 + \cos^2 \theta},$$  \hspace{1cm} (2)

the spin structure with the minimum energy for the system is the $q = 0$ type with the positive chirality and the spins direct to or from the center of the triangle on the kagomé
lattice. This means that the system corresponds effectively to the two-dimensional Ising antiferromagnet, which has the magnetic phase transition at finite temperature \[10\]. The ordering in the plane would induce the three-dimensional ordering due to the infinitesimal interplane interaction.

The relaxation rate in the ordered phase can be analyzed by the two-magnon process of the spin wave in the Heisenberg kagomé lattice antiferromagnet. The relaxation rate by the two-magnon process is expressed as \[11\],

\[
\frac{1}{T_1} = \frac{\pi}{2} \gamma^2 \gamma_n^2 \hbar^2 \sum_{i,j} G_{ij} \int_{\omega_0}^{\omega_m} \left\{ 1 + \left( \frac{\omega_m}{\omega} \right)^2 \right\} \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} N(\omega)^2 d\omega,
\]

where \(G_{ij}\) is the geometrical factor of the dipolar interaction, \(\omega_m\) is the maximum frequency, \(\omega_0\) is the energy gap and \(N(\omega)\) is the state density of magnons. The dispersion relation of magnons in the system of \(q = 0\) type spin structure has been obtained by Harris et al. \[7\]. We adapt their method for Fe jarosite by introducing the anisotropy. The dispersion curves have the energy gaps due to the anisotropy and the lowest energy gap is given as,

\[
\Delta \epsilon = S \sqrt{(3J + 2E + 2(E\cos^2\theta - D\sin^2\theta))(2(D - E) + 4(E\cos^2\theta - D\sin^2\theta))}. \tag{4}
\]

Applying the long wave approximation for the dispersion relation, the relaxation rate is given as \[12\],

\[
\frac{1}{T_1} = \frac{\pi}{2} \gamma^2 \gamma_n^2 \hbar^2 \sum_{i,j} G_{ij} \frac{9\hbar}{k_B (T_m^2 - T_0^2)} T^5 \int_{T_0/T}^{T_m/T} \left\{ x^2 - \left( \frac{T_0}{T} \right)^2 \right\} \left\{ x^2 + \left( \frac{T_m}{T} \right)^2 \right\} \frac{e^x}{(e^x - 1)^2} dx,
\]

where \(T_m = \hbar\omega_m/k_B\) and \(T_0 = \hbar\omega_0/k_B\). We calculated the temperature dependence of \(1/T_1\) and the calculated values are shown in Fig. \[4\] by the solid curve. The agreement between the experimental data and the calculated values is fairly well and we get the value of energy gap to be 25 K. The values of \(E\) and \(D\) are estimated by using Eq. \[2\] and \[4\] as,

\[
0.0012 < \frac{E}{J} < 0.020, \tag{6}
\]

\[
0 < \frac{D}{J} < 0.020. \tag{7}
\]
As is seen in Fig. 2, the susceptibility for Cr jarosite increases sharply below 4.2 K. Below this temperature the difference between the susceptibility measured after the zero-field cooling (ZFC) and that measured after the field cooling (FC) was observed. The same behavior has been reported by A. Keren et al. [13]. The magnetization curve was measured at 2.0 K to clarify this anomaly and is shown in Fig. 3. There we find a small hysteresis loop, which suggests the existence of weak ferromagnetic moments. The difference in the susceptibility between ZFC and FC comes from the hysteresis loop below 4.2 K. By our neutron diffraction experiment for Cr jarosite the long-range ordering has been observed below 4.2 K. S. -H. Lie et al. have also reported the weak long range antiferromagnetic ordering observed by the neutron experiments [14]. We conclude that the transition of Cr jarosite at 4.2 K is not a spin glass like but magnetic one.

The weak ferromagnetic moment is considered to be caused by the canting of the 120° arrangement perpendicular to the c-plane due to the anisotropy. On the other hand, the ferromagnetic moment was not observed for Fe jarosite. These results can be explained by the antiparallel stacking of the net moments on the c-plane for Fe jarosite and parallel stacking of the net moments for Cr jarosite. This is consistent with the result from the neutron experiments that the magnetic unit cell in Cr jarosite is equal to the chemical unit cell, while that in Fe jarosite is double the chemical unit cell along the c-axis.

IV. SUMMARY

In summary we have investigated the kagomé lattice antiferromagnets KFe$_3$(OH)$_6$(SO$_4$)$_2$ and KCr$_3$(OH)$_6$(SO$_4$)$_2$ by means of the magnetization, NMR and neutron experiments. The susceptibility data of these samples are well fitted with the susceptibility calculated by the high temperature expansion for the two-dimensional Heisenberg kagomé lattice antiferromagnet. Long range magnetic ordering occurs at 65 K for KFe$_3$(OH)$_6$(SO$_4$)$_2$. The spin structure in the ordered phase is the 120° structure with $q = 0$, +1 chirality and the direction being to or from the center of the triangle. The order is caused by the single-ion-type
anisotropy $D, E$. This system corresponds effectively to the two-dimensional Ising system, which has the two-dimensional ordering. The fluctuation in the ordered phase is caused by the spin wave. The nuclear spin-lattice relaxation is governed by the two-magnon process. For $\text{KCr}_3(\text{OH})_6(\text{SO}_4)_2$ magnetic transition occurs at 4.2 K. The transition is not spin-glass one but the magnetic ordering. The weak ferromagnetic moments are observed. This comes from the canted $120^\circ$ spin structure, and all net moments in the planes are parallel to the $c$-axis.
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FIG. 1. Temperature dependence of the susceptibility for KFe$_3$(OH)$_6$(SO$_4$)$_2$. 
FIG. 2. Temperature dependence of the susceptibility for $\text{KCr}_3(\text{OH})_6(\text{SO}_4)_2$. 
FIG. 3. Observed and calculated inverse susceptibility of KCr$_3$(OH)$_6$(SO$_4$)$_2$. The closed circles are experimental data of $\chi^{-1}$ under the external magnetic field 500 Oe. The result calculated from the high temperature series expansion up to the 8th order is shown by the dotted curve. The result obtained by Padé [4,4] approximants is shown by the solid curve. The broken curve shows the Curie-Weiss law.
FIG. 4. Proton spin-lattice relaxation rate of KFe$_3$(OH)$_6$(SO$_4$)$_2$. The closed circles are experimental data at 75.1 MHz. The solid curve shows the temperature dependence of $1/T_1$ calculated from the two-magnon process using the energy gap of 25 K.
FIG. 5. Magnetization curve of KCr$_3$(OH)$_6$(SO$_4$)$_2$ at 2.0 K.