Effect of DM interaction in a quantum antiferromagnet on a deformed kagome lattice, Rb$_2$Cu$_3$SnF$_{12}$

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Abstract. We have performed $^{63,65}$Cu-NQR measurements of a quantum antiferromagnet on a deformed kagome lattice, Rb$_2$Cu$_3$SnF$_{12}$. The spin-lattice relaxation rate $T_1^{-1}$ of $^{63}$Cu decreases steeply below 50 K. The rate shows no magnetic ordering down to 1.3 K and the existence of an energy gap. The temperature dependence of $T_1^{-1}$ between 10 and 50 K is expressed by an Arrhenius-type function, with which the gap energy was estimated to be 50 K. This value is rather large compared to the value of 21 K obtained from the magnetic susceptibility and magnetization measurements. This difference can be ascribed to the dispersion of triplet excitations due to Dzyaloshinsky-Moriya (DM) interaction and four different antiferromagnetic (AF) interactions. A large state density in the triplet state with the dispersion gives a significant effect on the spin fluctuation. Eight peaks were observed between 45 and 55 MHz in $^{63,65}$Cu-NQR spectra at 5 K. These peaks correspond to two isotopes and four crystallographic sites of Cu. This result implies that a crystal structure with two Cu sites at room temperature changes to a structure that has four Cu sites below the structural phase transition at 215 K.

1. Introduction

Antiferromagnets on the Kagome lattice have fascinating properties due to the geometrical frustration. A classical antiferromagnet on the Kagome lattice has continuous degeneracy, even at zero temperature. However, it is predicted that the co-planar 120° spin configuration with $\sqrt{3} \times \sqrt{3}$ structure is preferred due to thermal fluctuations: that is, order by disorder [1]. On the other hand, for quantum spins, it has been theoretically demonstrated that the ground state is singlet with a spin gap to the magnetic triplet excited state. This gap is continuously filled with nonmagnetic singlet states [2]. It has also been proposed that there is a nondispersive excited state in both classical and quantum spins [3, 4]. When the kagome lattice is deformed and has different exchange interactions, the excited states have a large dispersion [5].

Kagome lattice antiferromagnets inherently have an antisymmetric Dzyaloshinsky-Moriya (DM) interaction, since there is no inversion center in the middle of two neighboring spins. The
Figure 1. Exchange interaction network on a deformed kagome lattice, Rb$_2$Cu$_3$SnF$_{12}$. $J_1 = 234$ K, $J_2 = 211$ K, $J_3 = 187$ K and $J_4 = 108$ K [8].

DM interaction is described by [6, 7]

\[ H_{DM} = \sum_{\langle i,j \rangle} D_{ij} \cdot (S_i \times S_j). \]  \(1\)

Here $D_{ij}$ is the DM vector, obtained from a second-order perturbation of the spin-orbit interaction and antiferromagnetic (AF) interaction, and its direction is determined by the symmetry of the crystal structure. The DM interaction breaks the rotational symmetry of the Heisenberg spin system. The triplet excited state split into $S_z = 0$ and $S_z = \pm 1$ due to the DM interaction as $\langle S_z = 0 | H_{DM} | S_z = 0 \rangle \neq 0$ and $\langle S_z = \pm 1 | H_{DM} | S_z = \pm 1 \rangle = 0$. Since the DM interaction does not break time reversal symmetry, it does not lift the degeneracy of $S_z = \pm 1$.

Here we present NQR studies of a quantum kagome antiferromagnet, Rb$_2$Cu$_3$SnF$_{12}$, to clarify the effects of DM interaction in a quantum antiferromagnet.

The crystal structure of Rb$_2$Cu$_3$SnF$_{12}$ is hexagonal with space group $R\bar{3}$ at room temperature [8]. CuF$_6$ octahedra are linked in the c-plane by sharing corners, and elongated along the principal axes, which are approximately parallel to the c-axis. Magnetic Cu$^{2+}$ ions with $s = 1/2$ are located at the center of the octahedra and form a kagome lattice in the c-plane. Since there are four different bond angles in the exchange pathway Cu$^{2+}$−F$^-$−Cu$^{2+}$ in this compound, Cu$^{2+}$ ions interact through four different antiferromagnetic interactions, $J_1 = 234$ K $> J_2 > J_3 > J_4 = 108$ K as shown in figure 1 [8]. Consequently, this system is regarded as a deformed kagome lattice antiferromagnet. The magnetic susceptibility decreases steeply at temperatures below 50 K, and magnetic ordering has not been observed down to 1.3 K [8]. Therefore, the ground state of this compound is considered to be a singlet with a spin gap. Because of the configuration of the strongest interaction $J_1$, this singlet state is considered to be a pinwheel valence-bond solid state [5]. A recent inelastic neutron scattering experiment has demonstrated that DM interaction plays an important role in the dispersion of triplet excitations [9]. In order to obtain microscopic informations regarding the effects of the DM interaction in the quantum antiferromagnet, we have performed $^{63,65}$Cu-NQR on a single crystal of Rb$_2$Cu$_3$SnF$_{12}$. 

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2. Experimental Procedures
The detailed sample synthesis are shown in ref. 8. The $^{63,65}$Cu NQR measurements of a single crystal were performed by a coherent pulsed spectrometer at zero field between 2 and 50 K. The oscillation field was applied perpendicular to the c-axis by a coil wound around the sample. The spin echo signals were measured at frequencies between 45 and 55 MHz to obtain the NQR spectrum. The spin-lattice relaxation rates $T_1^{-1}$ were obtained from the recovery of the spin echo signals after the saturation pulses.

3. Results and Discussions
Figure 2 shows the $^{63,65}$Cu-NQR spectrum at 5.2 K. Eight resonance peaks were observed. These peaks correspond to resonance with the nuclear quadrupole splitting, since there are neither an applied field nor an internal field. The nuclear quadrupole Hamiltonian is written as

$$H_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[ (3I_z^2 - I^2) + \eta \frac{I_x^2 + I_y^2}{2} \right],$$

where $I$ is the nuclear spin with $I = 3/2$ for both $^{63}$Cu and $^{65}$Cu, $Q$ is the nuclear quadrupole moment, $^{63}Q = -0.211 \times 10^{-29} \text{ m}^2$ and $^{65}Q = -0.195 \times 10^{-29} \text{ m}^2$, respectively, $V_{\alpha\alpha} = \frac{\partial^2 V}{\partial \alpha^2}$, $\alpha = x, y, z$ are the electric field gradients, where $V$ is the electrostatic potential at the nuclear site, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter. The Hamiltonian $H_Q$ can be diagonalized, and the NQR frequency $\nu_Q$ corresponding to the transition $I_z = \pm 1/2 \leftrightarrow \pm 3/2$ is obtained to be

$$\nu_Q = \sqrt{1 + \frac{\eta^2}{3} \times \frac{3eQ|V_{zz}|}{2I(2I-1)\hbar}}.$$

The four peaks at $\nu_Q = 49.8, 51.1, 52.8, \text{ and } 53.5 \text{ MHz correspond to } ^{63}\text{Cu resonances, and the rest four peaks at } \nu_Q = 46.0, 47.1, 48.8, \text{ and } 49.4 \text{ MHz correspond to } ^{65}\text{Cu resonances. Since } \nu_Q \text{ depends on } Q \text{ and the electric field gradient parameters, } |V_{zz}| \text{ and } \eta, \text{ the observed
eight peaks could correspond to two isotopes with different quadrupole moments and four crystallographic Cu sites at which the electric field gradients are different. The crystal structure at room temperature has two kinds of Cu sites, and the structural phase transition at $T_S = 215$ K can be observed by X-ray diffraction [9, 10] and specific heat measurements [11]. However, the detailed crystal structure below $T_S$ has not yet been determined so far. The NQR spectra indicate that the crystal structure below $T_S$ should have four Cu sites.

Figure 3 shows the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ of $^{63}$Cu on the site with the largest electric field gradient at 53.5 MHz. The recovery of nuclear magnetization above 10 K was expressed by a single exponential function. By contrast, the recovery of nuclear magnetization below 10 K was expressed by a stretched exponential function with $\beta < 1$, as

$$
\frac{M(\infty) - M(t)}{M(\infty)} = \exp\left( -\left( \frac{t}{T_1} \right)^\beta \right).
$$

When $\beta = 1$, equation (4) is a single exponential function. Since $\beta < 1$, the recovery process below 10 K is considered to become inhomogeneous. The rate decreases steeply below 50 K ($T^{-1} = 0.02 \text{ K}^{-1}$) and shows no critical divergence down to 2 K. This indicates that there is no magnetic ordering down to 2 K. When a gap energy $\Delta$ contributes to the relaxation process, the relaxation rate $T_1^{-1}$ at $T \ll \Delta$ is proportional to an Arrhenius-type function [12],

$$
\frac{1}{T_1} \propto \exp\left( -\frac{\Delta}{T} \right).
$$

The temperature dependence of $T_1^{-1}$ between 10 and 50 K indicates a gap energy of 50 K. Below
$J_1 = 18.6 \text{ meV}$, $d_{iJ} = 0.18 J_i$
$J_2 = 0.95 J_i$ (for $i = 1 \sim 4$)
$J_3 = 0.85 J_i$
$J_4 = 0.55 J_i$

\[ E_0 = \pm z S_1 \pm z S_2 \pm 20K \pm 50K \]

**Figure 4.** The dispersion of a triplet excitation obtained from the dimer series expansion of the pinwheel VBS state from ref. 9. The inset shows the Brillouin zone of the kagome lattice.

At 10 K, the temperature dependence of $T^{-1}$ becomes weak. This behavior may be ascribed to the effect of relaxation due to impurity spins, since the recovery process becomes inhomogeneous below 10 K. Therefore the rate below 10 K may not reflect the intrinsic relaxation process.

The gap energy estimated from $T^{-1}$ is rather large compared to the value of 21 K obtained from magnetic susceptibility and magnetization measurements [8]. This difference can be explained by the dispersion of the excited states, calculated theoretically by a dimer series expansion of the pinwheel VBS ground state using the Hamiltonian, which involves four different AF interactions and the DM interaction [9]. An illustration of the calculated dispersion is shown in figure 4. The splitting of the triplet excitation between $S_z = 0$ and $S_z = \pm 1$ is due to DM interaction and the large dispersions are derived from four AF interactions. As the relaxation rate $T^{-1}$ depends on the state density of excitations, the NQR results between 10 and 50 K correspond to a magnetic excitation with a large state density with the gap energy 50 K. These excitations correspond to the excitations between the M-point and the K-point with flat dispersions in figure 4. On the other hand, the magnetic susceptibility at low temperatures is dominated by magnetic excitations with a minimum energy gap around the $\Gamma$-point.

In summary, a DM interaction and four different AF interactions produce a significant effect on the triplet excitation of a quantum antiferromagnet on a deformed Kagome lattice. Four AF interactions result in a large dispersion of the triplet excitation, and the DM interaction induces a splitting of the triplet excitation between $S_z = 0$ and $S_z = \pm 1$. The excitations with a large state density in the triplet state strongly affect the spin fluctuation, which arises a large relaxation of the nuclear spins.

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