Cs-NMR Study on the Ground State of the Equilateral Triangular Spin Tube CsCrF$_4$

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Abstract. We have investigated the hyperfine coupling between Cs and Cr on the $S = 3/2$ equilateral triangular spin tube CsCrF$_4$, utilizing $^{133}$Cs-NMR. At paramagnetic state above 80 K, we have obtained spectra containing a single peak, which reflects the single crystallographic Cs site. From the temperature dependence of the peak shift and peak width, we evaluated effective values of the isotropic and the anisotropic part of hyperfine coupling. The latter was compared with the calculated dipole contribution. Using obtained parameters with assumed spin structure, we tried to reproduce the broadened spectrum in the ordered state at 2.0 K. The preliminary analysis shows the 120-degree structure does not accord with the observed spectra at the ordered state.

1. Introduction

$S = 3/2$ spin tube compound CsCrF$_4$ consists of equilateral triangles of Cr$^{3+}$, stacked along $c$-axis without twisting. Tubes are separated by Cs atoms, forming a rhombic unit cell. The schematic structure (the space group $P6_2/m$ [1]) is shown in Fig. 1.

From the theoretical viewpoint, the ground state of the equilateral triangular spin tubes has been argued to have the gapped ground state. For the system with $S = 1/2$, the gap opens up by arranging the singlet dimers on the leg and rung direction [2, 3]. As for the $S = 3/2$ system, though the size is smaller than $S = 1/2$ system, the gap opens by forming singlet dimers in a similar way [4].

The synthesis of this compound was first reported in 1978 [1]. In 2009, Manaka et al. have reported its magnetic properties, such as uniform susceptibility, ESR and heat capacity [5, 6]. He argued that there is no magnetic order at low temperatures down to 1.5 K and that its ground state is the gapless spin-liquid. Quite recently, our group has reported the existence of a magnetic phase transition with $T_N \simeq 5.0$ K by the spectral broadening of NMR experiments [7]. Thus, CsCrF$_4$ is expected to be one of the simplest model compound of a playground of geometrical frustration and low-dimensionality.

Sofar, the spin exchange interactions were evaluated by the density functional theory calculation [8]. The dominant interactions are antiferromagnetic, that is, $J_{\text{rung}} = -19$ K for the triangular plane, $J_{\text{chain}} = -39$ K for the tube direction and $J_{\text{inter}} = -3.2 \times 10^{-3}$ K for the inter-tube exchange interaction.
Recently, Seki *et al.* suggested an interesting approach with an inter-tube coupling. The spin tube system can be treated as Kagomé-triangular lattice, which has the same lattice topology in the \(ab\)-plane [9]. Depending on inter-tube coupling, various ordered phases are expected such as 120-degree structure, incommensurate order, ferromagnetic order and cubic order, which has noncoplanar 120-degree spin structure.

Though there are many investigations theoretically and experimentally, the ground state of CsCrF\(_4\) is still unknown. Particularly, the spin structure in the possible ordered state is not determined. This is mainly because no reports with neutron scattering has been given until now. Instead, we try to investigate the magnetic structure by NMR. For this purpose, it is essential to determine the hyperfine coupling tensor [10]. The preliminary result on the hyperfine coupling tensor for \(^{19}\text{F}\) sites has been reported by us recently [11]. In this paper, we investigate the hyperfine coupling tensor for \(^{133}\text{Cs}\)-site. By using the obtained hyperfine coupling tensor, we have performed the preliminary analysis in the ordered state.

2. **Experimental**

The powder sample is prepared by the conventional solid-state reaction method [5, 6]. \(^{133}\text{Cs}\)-NMR spectra were measured in a wide temperature range between 2 and 300 K, under magnetic field around 5.67 T. The Cs site is located on interstitial position between tubes, and between CrF\(_3\) layers. NMR spectra were obtained by recording the spin-echo amplitude against magnetic field, which was slowly varied within a narrow region around zero shift position [12, 13].

3. **Results and Discussion**

The typical profile of \(^{133}\text{Cs}\)-NMR spectra measured in various temperatures between 80 and 300 K are shown in Fig. 2. We have observed a single peak, which may reflect the single crystallographic site of \(^{133}\text{Cs}\). The electrical quadrupole splitting \(^{133}Q/^{133}\gamma\) is estimated to be smaller than 50 Oe. The spectral shape was slightly asymmetric as compared to Gaussian function. We treated this asymmetry in the terms of the uniaxial anisotropy to obtain the anisotropic part of Knight shift. This assumption is reasonable for the local symmetry around the

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Figure 1. Schematic drawings of CsCrF\(_4\) structure (a) on \(ab\)-plane and (b) along \(c\)-axis. Dashed lines show the unit cell. Cs atoms are located at interstitial positions between tubes.
Cs site (Fig. 1). We evaluated the peak shift from the peak position $H_{\text{peak}}$ as $^{133}\nu Q/^{133}\gamma - H_{\text{peak}}$. The peak shift decreases with increasing temperature. In Fig. 3 and Fig. 4, we show the temperature dependence of peak shift $\Delta H$ and full width at half maximum (FWHM) of the peak with that of the uniform susceptibility.

From these scaling plots, the coupling constants of the isotropic component of hyperfine coupling $A_{\text{iso}}$ and the anisotropic component $A_{\text{an}}$ were obtained to be $1000 \pm 50 \, \text{G}/\mu_B$ and $60 \pm 40 \, \text{G}/\mu_B$, respectively. Note that the latter includes both the contribution from the hyperfine coupling and the dipole-dipole coupling, and is too small compared with the contribution of dipole-dipole coupling, which was obtained by the calculation based on the classical dipole-dipole interaction as $A_{\text{dip}} = 412 \, \text{G}/\mu_B$. This means that the contribution of the superexchange interaction via F ion of $350 \pm 40 \, \text{G}/\mu_B$ must exist, for the case that the principal axes of the two contributions are assumed to be identical.

Next, we try to reproduce the spectrum in the ordered state with these hyperfine coupling constants. The considerably large value $J_{\text{chain}}$ and the three-fold symmetry invoke one, as the simplest assumption, the $q = 0$ 120-degree structure in $ab$-plane with antiferromagnetic structure along the tube direction. Before reproducing spectrum, we refer to contribution of hyperfine coupling in this ordered state. In this structure, the contribution of hyperfine coupling is geometrically canceled at Cs site due to antiferromagnetic two spins along the tube direction, so we can calculate the internal field by adding up the contribution of classical dipole-dipole interaction. We put at each Cr site an ordered moment with direction according with the 120-degree structure with chirality +1. The summation for the Cr site was taken for those with in the radius 400 Å. The simulated powder pattern is shown in Fig. 5. It is a single component of flat-topped shape, which reflects the fact that there is a unique magnetic $^{133}\text{Cs}$ site in the assumed spin structure. This does not accord with the observed $^{133}\text{Cs}$-NMR spectrum at 2.0 K, irrespective of the assumed moment size. The latter consists of the two components, sharp center peak and shoulders at both sides, which indicates that there exist the two Cs sites in the unit cell.
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Figure 4. Temperature dependence of the peak width (open circle) and the uniform susceptibility (solid line) [5].

Figure 5. Calculated and observed $^{133}$Cs-NMR spectrum in an ordered state at 2.0 K. Calculation is based on 120-degree structure with the effective magnetic moment of Cr$^{3+}$, 3.84µB [6]. Dashed curve denotes the calculated spectrum convoluted with Gaussian width of 0.05 T.

4. Summary
We have investigated the hyperfine coupling between Cs and Cr on the $S = 3/2$ equilateral triangular spin tube CsCrF$_4$, utilizing $^{133}$Cs-NMR. At paramagnetic state, we have obtained the isotropic and anisotropic parts of hyperfine coupling as $A_{iso} = 1000 \pm 50$ G/µB and $A_{an} = 60 \pm 40$ G/µB, respectively. We also calculated the dipole coupling tensor contributing to the anisotropy in the hyperfine coupling, $A_{dip} = 412$ G/µB. By using these parameters, and by assuming the spin structure, we tried to reproduce the spectrum in the ordered state. The 120-degree structure was tested, and was found to disagree with the observation. In order to find a spin structure that matches the NMR observation, one has to assume the structure containing two inequivalent Cs sites, such as $q = 1/2$ within $ab$-plane or $\chi = -1$. Work is in progress to simulate NMR spectra for this structure.

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