

The magnetic structure on the ground state of the equilateral triangular spin tube

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Abstract The ground state of the frustrated equilateral triangular spin tube CsCrF_4 is still hidden behind a veil though NMR spectrum broaden into 2 T at low temperature. In order to investigate the spin structure in an ordered state by ^{19}F -NMR, we have determined the anisotropic hyperfine coupling tensors for each three fluorine sites in the paramagnetic state. The measurement field was raised up to 10 T to achieve highest resolution. The preliminary analysis using the obtained hyperfine tensors has shown that the archetypal 120° -type structure in ab -plane does not accord with the NMR spectra of ordered state.

Keywords Triangular spin tube · NMR · Frustration

1 Introduction

The odd-leg spin tube antiferromagnets have attracted much attention recently, because the geometrical frustration and one-dimensionality lead to suppress ordering and may bring an exotic ground state. So far, three-leg spin tube of $S = 1/2$ and $S = 3/2$ is theoretically investigated. The former has been reported have a gapped ground state in a finite region of

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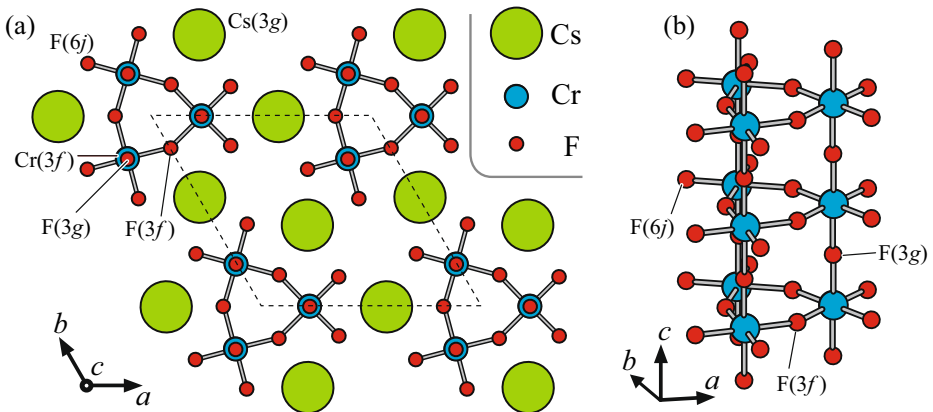


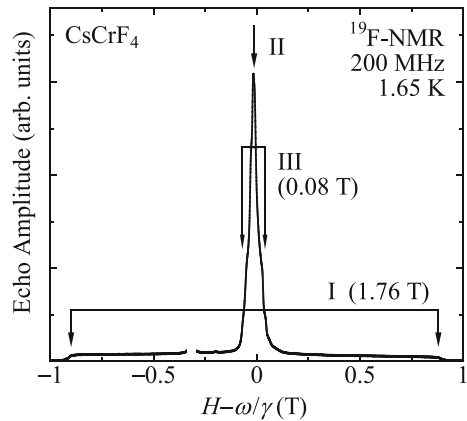
Fig. 1 Schematic drawings of CsCrF_4 crystal structure ($P\bar{6}2m$) (a) on ab -plane, and (b) along c -axis. The unit cell is shown by dashed line

triangle distortion [1]. As for the latter, the system may also be in the gapped state with an exquisite arrangement of singlet dimers on rungs and legs. The gap size may be so small that it will be invisible through experiments [2]. Experimentally, some model compounds have been investigated such as the nine-leg $\text{Na}_2\text{V}_3\text{O}_7$ with C_3 -symmetry [3–6] or the three-leg spin tube $[\text{CuCl}_2(\text{tachH})_3\text{Cl}]\text{Cl}_2$ with the twisted legs [7, 8]. However, these compounds can not be treated a simple tube due to their complex exchange paths.

The title compound CsCrF_4 is one of the simplest equilateral triangular spin tubes, consisting of Cr^{3+} ions (d^3 , $S = 3/2$), which form equilateral triangles in ab -plane, stacked along c -axis without twisting (Fig. 1), Cs^+ ions located at interstitial sites between tubes, maintaining the good one-dimensionality, and F^- ions, which have three inequivalent positions, $3f$, $3g$ and $6j$. The distances between each of these F ions and its nearest Cr^{3+} are 1.93, 1.92 and 1.80 Å, respectively. According to the density functional theory (DFT) calculation, the spin exchange interaction J_\perp for the triangular ring and J_\parallel along the tube are both antiferromagnetic, with $J_\perp/J_\parallel \simeq 0.5$, and the exchange interaction between adjacent tubes is negligibly small [9]. This DFT result implies the antiferromagnetic spin structure along tube direction in the ordered state. So far, the measurements of macroscopic quantities, magnetic susceptibility and heat capacity, suggest that the system has a gapless ground state and yet shows no magnetic order [10–12]. Quite recently, preliminary results of microscopic measurements NMR, μSR and neutron scattering report the existence of a magnetic phase transition [13, 14]. Especially, the last one suggests the magnetic q -vector $(1/2, 0, 1/2)$ and the archetypal 120° -type structure in ab -plane at low temperature of 1.7 K [13, 15].

However, except for these preliminary reports, the detailed spin state in the ordered state is not known until now. In order to investigate its spin structure by NMR, knowledge of the hyperfine coupling constants is imperative. Particularly, for F-sites, their internal fields are contributed both from the classical dipole-dipole interaction and from the hyperfine interaction, so that one must determine the coupling constants experimentally. For this purpose, we studied the paramagnetic spectra taken at highest field of 10 T, which is expected to give higher resolution than our previous report [14], and have successfully determined the hyperfine coupling tensors for each three fluorine sites.

Fig. 2 F-NMR spectrum at 1.65 K, where the system is expected to be in a magnetically ordered state. The spectrum consists of three parts, a wide plateau #I, a sharp peak #II and a broad peak #III, which are shown by arrows. The widths between the edges at both sides for #I and #III are also shown. The center field ω/γ is 4.99 T



2 Experimental detail

The powder sample of CsCrF₄ was obtained by the conventional solid-state reaction method, and was annealed in HF gas [10, 11]. Its crystal structure belongs to the space group of *P62m* with lattice constants $a = 9.619 \text{ \AA}$, $c = 3.847 \text{ \AA}$ [10]. NMR measurements were performed in the field region between 4 and 10 T and the temperature region between 1.6 and 120 K. Spectra were obtained by recording the spin-echo amplitude against magnetic field.

3 Result and discussion

First, we show in Fig. 2 an overall view of the ¹⁹F-NMR spectrum of powder sample measured at 1.65 K. At this temperature, the system is expected to be in the ordered state. The spectrum consisted of three parts, a wide plateau #I, a sharp peak #II and a broad peak #III, corresponding to the three F-sites. The subject of this paper is to determine the hyperfine coupling tensors of F sites for the analysis of this spectrum. Figure 3 shows typical spectra in the paramagnetic state. Note that the three peaks #1, #2 and #3 show a characteristic profile for uniaxial anisotropy. ΔH^\perp and ΔH^\parallel , the peak and edge point of the powder pattern of uniaxial system are successfully assigned to the observed spectrum.

In this system, for each three F sites, the local symmetry is approximately uniaxial, and the principal axis of classical dipole-dipole interaction tensor is nearly parallel to the F–Cr bond direction, and hence to the principal axis of hyperfine tensor. In this situation, ΔH^\perp and ΔH^\parallel can be formulated as follows,

$$\begin{cases} \Delta H^\perp(\alpha) = (-A_{\text{ani}}^{\text{dip}}(\alpha) - A_{\text{ani}}^{\text{HF}}(\alpha) + A_{\text{iso}}^{\text{HF}}(\alpha)) \cdot \chi(T)H_0 \\ \Delta H^\parallel(\alpha) = (2A_{\text{ani}}^{\text{dip}}(\alpha) + 2A_{\text{ani}}^{\text{HF}}(\alpha) + A_{\text{iso}}^{\text{HF}}(\alpha)) \cdot \chi(T)H_0 \end{cases} \quad (1)$$

where α is $3f$, $3g$, or $6j$, $\chi(T)$ is the uniform susceptibility, H_0 is magnetic field, and $A_{\text{ani}}^{\text{dip}}(\alpha)$, $A_{\text{ani}}^{\text{HF}}(\alpha)$ and $A_{\text{iso}}^{\text{HF}}(\alpha)$ are the coupling constants of the anisotropic component of dipole coupling, the anisotropic component of hyperfine coupling and the isotropic component of hyperfine coupling, respectively. $A_{\text{ani}}^{\text{dip}}(\alpha)$ for each F-site was obtained by a simple calculation based on the classical dipole-dipole interaction, and shown in Table 1.

Fig. 3 Typical spectrum in the paramagnetic state. The observed three peaks and corresponding edges, denoted as #1, #2 and #3, are shown by solid and dashed arrows, respectively

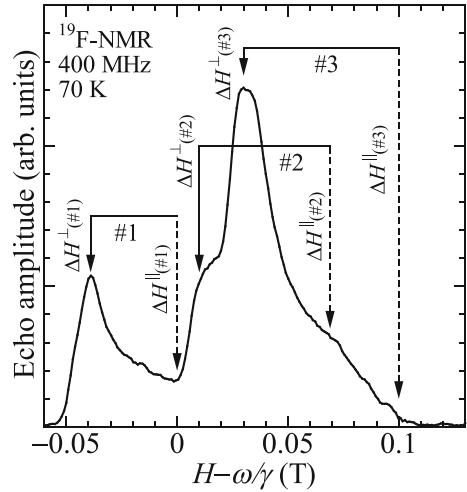


Table 1 The coupling constants for each F-site

F-site	$A_{\text{ani}}^{\text{dip}}$ (T)	Case A (#1 = 3 <i>f</i>)		Case B (#1 = 3 <i>g</i>)	
		$A_{\text{ani}}^{\text{HF}}$ (T)	$A_{\text{iso}}^{\text{HF}}$ (T)	$A_{\text{ani}}^{\text{HF}}$ (T)	$A_{\text{iso}}^{\text{HF}}$ (T)
3 <i>f</i>	+0.205	-0.295	+0.200	-0.297	-0.170
3 <i>g</i>	+0.258	-0.350	-0.170	-0.348	+0.200
6 <i>j</i>	+0.161	-0.290	-0.310	-0.290	-0.310

From calculated $A_{\text{ani}}^{\text{dip}}(\alpha)$ and observed values of ΔH^{\perp} and ΔH^{\parallel} , we have determined $A_{\text{ani}}^{\text{HF}}(\alpha)$ and $A_{\text{iso}}^{\text{HF}}(\alpha)$ for the three F sites, using Eq. 1 and shown them in Table 1. Note a considerable amplitude of for the anisotropic component $A_{\text{ani}}^{\text{HF}}(\alpha)$ for all the three F sites. This may come from the fact that F–Cr bonds are borne by *p*-orbital. Considering the stoichiometric ratio, the peak #3, which has the largest amplitude, was safely assigned to 6*j* site. However, we could not determine the correspondence between the other two sites. Therefore, we include two sets of parameters in Table 1 for the two possible cases A and B, where 3*f* and 3*g* are assigned to #1 and #2, or #2 and #1, respectively. By using these obtained coupling constants and the value of $\chi(T)$ [10], we have reproduced the temperature dependence of ΔH^{\perp} and ΔH^{\parallel} for all the F sites and shown in Fig. 4, where one can see a good agreement. We also calculated the spectrum of 60 K to find an excellent agreement between experiment and calculation (Fig. 5).

Next, we try to reproduce the spectrum in the ordered state with these hyperfine coupling constants. This will test the reported *q*-vector (1/2, 0, 1/2) and the spin structure [15]. The antiferromagnetic structure along the leg direction expected from the *q*-vector indicates that the internal magnetic field at 3*g* site is uniquely the dipole interaction, because the field brought by the hyperfine interaction is geometrically cancelled. At 3*f* and 6*j* site, the internal field consists of both the dipole field and the hyperfine field. In the ordered state, each site of 3*g*, 3*f* and 6*j* will show a symmetric flat powder pattern with a width of $2\Delta H(\alpha)$, where $\Delta H(\alpha)$ is the size of the internal field at each site. In calculating $\Delta H(\alpha)$,

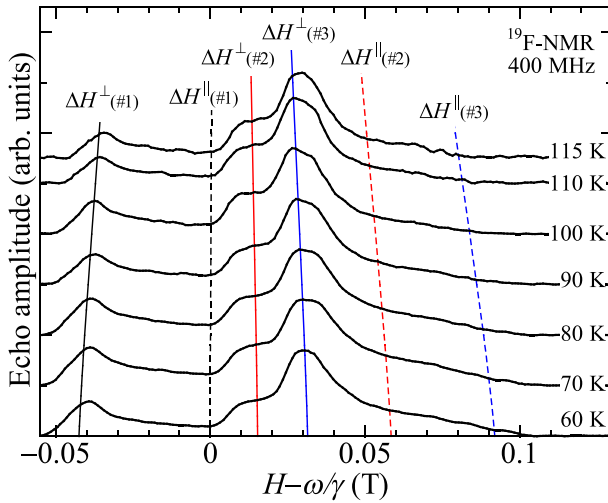
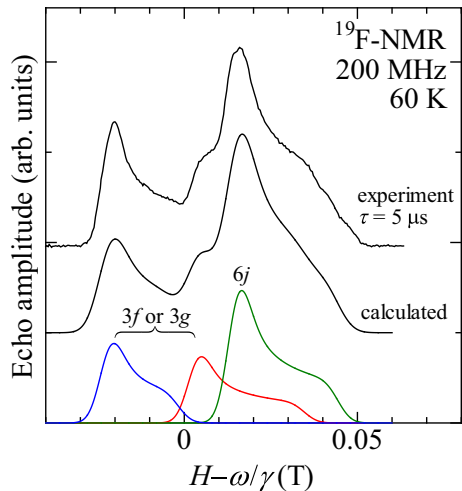


Fig. 4 Profiles of spectra at various temperatures. The vertical solid and dashed curves show the expected peak or edge positions calculated from the magnetic susceptibility [11] and hyperfine coupling constants with Eq. 1

Fig. 5 The observed F-NMR spectrum at 60 K and the calculated pattern based on the obtained hyperfine coupling constants in Table 1. To show the stoichiometric ratio of three F sites as it is, the spectrum taken with the shortest τ is shown. In the calculation, Gaussian width of 0.007 T is convoluted. At the bottom, we show the contribution from each three F sites separately



we put at each i -th Cr site an ordered moment $\vec{\mu}_i$ with direction according with the 120° -type structure with chirality $+1$, and with an assumed size μ_0 . Then $\Delta H(\alpha)$ is immediately calculated by using the hyperfine tensor $A_i(\alpha)$ as $\Delta H(\alpha) = |\sum_i A_i(\alpha)\vec{\mu}_i|$ and is ready to be compared with the ordered state spectrum in Fig. 2. The summation i was taken for those with in the radius 500 \AA for $A_{\text{ani}}^{\text{dip}}(\alpha)$, and only for the nearest neighbor for $A_{\text{ani}}^{\text{HF}}(\alpha)$ and $A_{\text{iso}}^{\text{HF}}(\alpha)$. With a constraint that μ_0 should be reasonable value, one notes that $3g$ must solely be assigned to #III, giving $\mu_0 = 1.1\mu_B$. However, with this μ_0 value, #II, the central narrow peak can neither be reproduced by $3f$ nor $6j$. Thus, one reaches a conclusion that the spin structure is not of the archetypal 120° -type.

Finally this argument has only denied one possible spin model. In order to determine the spin structure of this system, tests on many other models are necessary, and are now in progress.

4 Summary

We have investigated the ground state and the paramagnetic state of CsCrF_4 by ^{19}F -NMR. We have determined the anisotropic hyperfine coupling tensors for each three fluorine sites in the paramagnetic state. Thorough reproducing the spectrum at ordered state with obtained constants, we have found that the archetypal 120° -type structure in ab -plane, does not accord with the NMR spectra of ordered state.

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