High-field ESR study on anomalous magnetization in CsFeCl3

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M. Chiba[a,b], Aripin[b], K. Kitai[b], S. Mitsudo[c], T. Idehara[c], S. Ueda[a], M. Toda[d,1]

[a]*Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan*
[b]*Department of Applied Physics, Fukui University, Fukui 910-8507, Japan*
[c]*Research Center for Development of Far Infrared Region, Fukui University, Fukui 910-8507, Japan*
[d]*Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan*

Abstract

In $CsFeCl_3$, an anomalous magnetization has been observed under the magnetic field exceeding 33 T applied parallel to the crystal c-axis, which cannot be explained within the framework of the fictitious spin $S = 1$. In order to clarify the nature of the anomalous magnetization, which is possibly due to the ground-state crossover with the excited state $S = 2$, an ESR experiment was performed under magnetic fields up to 40 T by use of a pulse magnet. The submillimeter wave around 300 GHz was supplied by Gyrotron FU IV at Research Center of Far Infrared Region, Fukui University. In the operation frequency of 301 GHz absorption lines have been observed corresponding to the anomalous magnetization jump.

Keywords: High-field ESR; High-field magnetization; $CsFeCl_3$; Fictitious spin; Ground-state crossover

1. Introduction

The magnetic crystal $CsFeCl_3$ is an interesting material as one of the families of ABX_3-type hexagonal crystal relating to the magnetic frustration caused by the triangular-lattice antiferromagnetism. Usually, the Fe^{2+} spin system in this material is treated within the framework of the fictitious spin $S = 1$ [1,2]. At zero magnetic field, the spin states are composed of the singlet ground and doublet excited states separated by D due to the crystallographic anisotropy. It is also interesting that the material does not have any long-range order at zero magnetic field. On the other hand, under a magnetic field $\boldsymbol{B}$ applied parallel to the crystal c-axis ($\boldsymbol{B} \| c$-axis), one of the states of the doublet excited state comes down to cross the ground state at 7.5 T. It is reported that the long-range magnetic order occurs around the level cross field below 2.5 K [3,4].

A high-field magnetization has been observed at 1.3 K with $\boldsymbol{B} \| c$-axis by one of the authors [5]. The magnetization increases rapidly with increasing magnetic field from about 4 to 11 T followed by a slight linear increase in the magnetization in the region between 0 and 4 T. The magnetization seems to saturate at 11 T. However, an anomalous magnetization has been observed under higher magnetic field B_c around 33 T [5]. The presence of the anomalous magnetization suggests the appearance of a new type of magnetic structure, which cannot be explained within the framework of the fictitious spin $S = 1$.

In order to clarify the nature of the above-mentioned anomalous magnetization, an ESR experiment was performed under magnetic fields up to 40 T. The ESR experiment has an advantage that a direct observation is possible on the behavior of the electronic spin states.

2. High-Field ESR

An ESR experiment was performed under magnetic fields up to 40 T by use of a pulse magnet with operating frequencies around 300 GHz. The experiment was performed at Research Center of Far Infrared Region, Fukui University.

2.1. *Submillimeter wave source*

The submillimeter wave around 300 GHz was supplied by Gyrotron FU IV operating in the superconducting solenoid up to 12 T. A typical cw operation mode of the gyrotron at the frequency of 301 GHz was TE_{03} mode with the output power of 20 W. The submillimeter wave was guided to the specimen by a light pipe. The absorption signal was detected by an InSb hot electron detector operating at the liquid-helium temperature.

2.2. *Pulsed magnetic field*

The pulsed magnetic field up to 40 T was generated by a pulse magnet driven by a capacitor bank of 30 kJ. The magnet is immersed in the liquid nitrogen. The bore where the magnetic field is generated was 12 mm in diameter. An insert Dewar was settled inside the magnet for cooling down the specimen by use of the liquid helium. The inner diameter of the insert Dewar at the center of the magnet was 7.6 mm.

2.3. *Results of ESR experiment*

The ESR experiment was carried out at 4.2 K with an operating frequency of 301 GHz. A pulse magnetic field was applied parallel to the c-axis of

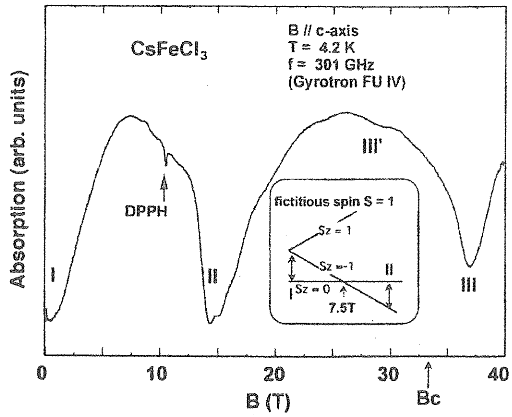

Fig. 1. High-field ESR in $CsFeCl_3$. $B \parallel c$-axis. B_c is the field where anomalous magnetization appears.

a single crystal $CsFeCl_3$. Three clear absorption lines I, II and III were observed as indicated in Fig. 1.

3. Spin state of Fe^{2+} in $CsFeCl_3$

The crystal structure of $CsFeCl_3$ belongs to the hexagonal crystal system [1] as shown in Fig. 2. The free ion state of $3d^6$ is ^5D. The energy levels are split by the effect of the crystalline field and the spin–orbit interaction (see Fig. 3). In the usual case only the lowest levels, namely, singlet ground and doublet excited states, are taken into account and are treated as the fictitious spin $S = 1$. The coupling J between Fe^{2+} ions along the chain is ferromagnetic, while the interchain coupling J' is antiferromagnetic, where $|J|/k \sim 7$ K and $|J'/J| \sim 0.05$ [2].

In order to consider the possibility that the excited state $S = 2$ crosses the ground state under the applied field, the single ion energy level scheme of Fe^{2+} is calculated with the following Hamiltonian [6]: $H = -k\lambda l \cdot S - \delta(l_z^2 - \frac{2}{3}) + \mu_B B(-kl_z + 2S_z)$ Here λ is the spin–orbit coupling energy, k the orbital reduction factor, and δ the magnitude of the trigonal distortion. The result is shown in Fig. 4, where the following parameters are used: $k = 0.9$, $|\lambda| = 103\ \text{cm}^{-1}$ and $|\delta/k\lambda| = 2$ [7]. The excited state $S_z = -2$ comes down with increasing magnetic field but never crosses the ground state $S_z = -1$.

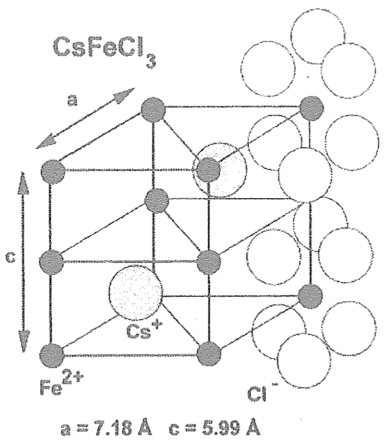

Fig. 2. Crystal structure of $CsFeCl_3$.

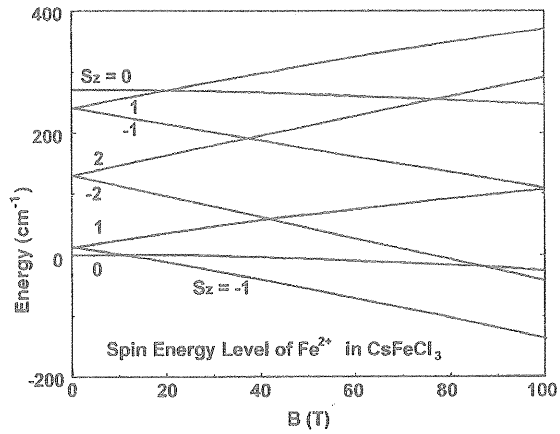

Fig. 4. Calculated electron spin energy level diagram of Fe^{2+} ion in $CsFeCl_3$. $B \parallel c$-axis.

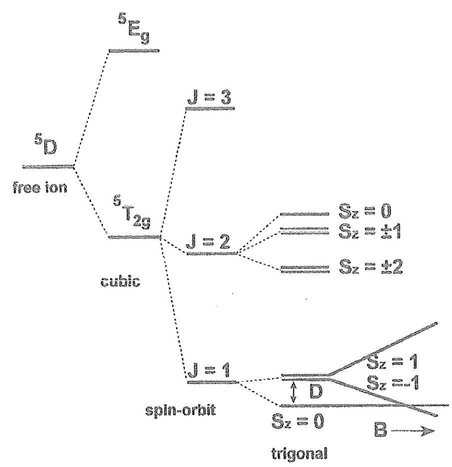

Fig. 3. Spin state of Fe^{2+} in $CsFeCl_3$.

4. Previous experiment of high-field magnetization

The present ESR experiment in $CsFeCl_3$ under high magnetic fields is motivated by an anomalous magnetization jump around 33 [5]. Here we briefly survey the high-field magnetization observed at 1.3 K with $B \parallel c$-axis.

Under the magnetic field from 0 to 4 T the magnetization is weak which shows that the ground state is singlet. The magnetization increases with increasing magnetic field from 4 to 11 T. The linear increasing of the magnetization in this region suggests the appearance of the magnetic order around the field of the ground-state crossover. These features are consistent with the theory by Tsuneto and Murao [8]. The magnetization seems to saturate at 11 T. Afterwards, up to about 32 T the magnetization is nearly constant, which is considered to be the saturation magnetization.

Thus below 32 T, the framework of the fictitious spin $S = 1$ has been found to work well for the explanation of the magnetization. However, under the magnetic field B_c around 33 T an anomalous magnetization has been observed. This behavior cannot be explained in the framework of the fictitious spin $S = 1$.

As far as the calculated energy level scheme in Fig. 4 is concerned, no anomalous effect is expected under the available magnetic field up to 40 T. One of the possible mechanisms of the anomalous magnetization is an intrachain (along c-axis) ferromagnetic coupling. The ion Fe^{2+} sees a large molecular field added to the applied magnetic field, which will enhance the lowering of the energy level of $S_z = -2$.

5. Discussion

In the experiment of ESR three clear absorption lines I, II and III were observed as indicated in Fig. 1. Lines I and II correspond to the transitions between the states $S_z = 0$ and -1 as indicated in the inset of Fig. 1. The experimental result of line I is consistent with the experiment carried out by other group [9,10]. The resonance fields are approximately 1 and 14 T for lines I and II, respectively. They are in the symmetric position with the center of 7.5 T of the level cross field.

Now we analyze the ESR lines I and II in the framework of fictitious spin $S = 1$ by using a single ion spin Hamiltonian, where the parameters D and g are modified by the exchange coupling. The Hamiltonian under the configuration of $B \| c$-axis ($\| z$) is given by $H = DS_z^2 + g\mu_B BS_z$. Here, $D(>0)$ brings a singlet ground and doublet excited states. The energy difference ΔE between the states $S_z = 0$ and -1 is written by $\Delta E = |g\mu_B(B - B_{cross})|$, where $B_{cross} = D/g\mu_B$. From the fact that the resonance fields of lines I and II are, respectively, 1 and 14 T, that $B_{cross} = 7.5$ T and that $\Delta E/h = 301$ GHz, g is estimated to be 3.3, which is not consistent with $g = 2.6$ estimated from the high-field magnetization [5]. The apparent large g estimated from the ESR result may be caused by the molecular field due to the intrachain ferromagnetic exchange coupling. The spin sees effectively the molecular field added to the applied field. As for the g-value estimated from the ESR result, $g = 2.54$ is reported [10] by the analysis based on the dynamical correlated-effective-field approximation [6]. However, in their analysis the appearance of the line II has not been expected.

Further, a strong absorption line named line III appeared at 37 T which is higher than 33 T of the anomalous magnetic jump field B_c. It is strange, because we expected that two resonance lines appeared at both lower and higher fields than the magnetization jump field, i.e., the field of the ground-state crossover. Actually, lines I and II appeared on both sides of B_{cross} in the case of low field.

The resonance fields of line III is by 4 T larger than $B_c = 33$ T, which corresponds to the g-factor of 5.3. The anomalously large g suggests the existence of the molecular field.

In the present case, line III is considered to be one of the lines appearing at the higher field than the crossover field B_c. What happens about the line below B_c? By examining Fig. 1 carefully we can find a broad absorption line named as III′ at 29 T. Line III′ might correspond to a resonance line below B_c. The line broadening may be due to the spin fluctuation and/or the exchange coupling.

According to the results of high-field magnetization [5] the value of the anomalous magnetization is a little larger than $4\mu_B/Fe^{2+}$. By assuming that g is about 2, the possible ground state is $S_z = -2$ at the field above 33 T. How does the state $S_z = -2$ come down?

At this moment we cannot have any definite answer. The frequency–field diagram will give the solution. ESR experiments under various operation frequencies is now in progress. The details of the ESR data will be presented in a separate paper.

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