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Field-angle dependence of the ice-rule breaking spin-flip transition in $Dy_2Ti_2O_7$

H Sato[1], K Matsuhira[2], T Sakakibara[1], T Tayama[1], Z Hiroi[1] and S Takagi[2]

[1] Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan
[2] Department of Electronics, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

E-mail: hide-s@issp.u-tokyo.ac.jp

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Abstract

Ice-rule breaking spin flip in the pyrochlore spin-ice compound $Dy_2Ti_2O_7$ has been studied in a field rotated in the $(1\bar{1}0)$ plane, by means of angle-resolved magnetization measurements. The field-angle dependence of the spin flip field $H_c(\theta)$ has been obtained. Close to the [111] direction, $H_c(\theta)$ exhibits a marked deviation from a nearest-neighbour spin-ice model, suggesting the importance of long-range dipolar interaction and a stability of the kagomé ice state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The rare-earth pyrochlore compounds $Dy_2Ti_2O_7$ and $Ho_2Ti_2O_7$, in which well localized spins reside on the vertices of corner-shared tetrahedra, have attracted much interest in recent years [1]. In these systems, a ferromagnetic interaction between spins leads to full frustration in the presence of strong single-ion Ising anisotropy along the $\langle 111 \rangle$ axes [2]. The stable spin configurations for each tetrahedron then obey the ice rule: two spins point outward and two spins inward ('two-in, two-out' state) in a basic tetrahedron [2]. This is exactly the same rule as the hydrogen bonding in the water ice obeys, and the systems are referred to as spin ice. Consequently, the ground state of the spin ice is highly degenerate and a static disordered state is formed at low temperatures whose residual entropy is very much like that of water ice [3]. Similar behaviour is also reported in $Ho_2Sn_2O_7$ [4, 5].

The ground-state degeneracy of the spin-ice state can be removed by applying a magnetic field that induces a finite magnetization M [2, 6–8]. The magnetizing process depends on the field direction [6, 7]. For H along [100] or [110] directions, M increases monotonically with H and saturates, maintaining the two-in, two-out structure. When H is applied along the [111] direction, the entropy releasing becomes a two-stage process. In a [111] magnetic field, the apical spin on the tetrahedra (spin D in figure 1) whose Ising axis is parallel to H first aligns, accompanied by a partial lifting of the degeneracy. Spin configurations on the

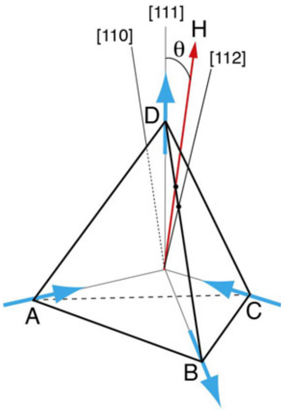

Figure 1. The stable two-in, two-out spin configuration of a unit tetrahedron in a field H slightly canted away from [111] towards the [112] direction at an angle $\theta(>0)$. The spin B on the basal plane has a component antiparallel to H and undergoes a flip when the Zeeman energy overcomes the magnetic interaction with neighbouring spins. When H is tilted towards the [110] direction ($\theta < 0$), spin B points inward whereas either spin A or spin C points outward.

basal plane constituting a kagomé lattice are, however, still macroscopically degenerate under the two-in, two-out ice rule; one of the spins A–C in figure 1 has a component antiparallel to H and is randomly distributed in the basal triangle. This intermediate state with a finite residual entropy is called 'kagomé ice' [9, 10]. As the field increases further, a spin flip to a fully polarized three-in, one-out (one-in, three-out) state occurs at ∼1 T when the Zeeman energy overcomes the magnetic interaction. Interestingly, this spin flip turns into a first-order transition of liquid–gas type below the critical end point $T_{\mathrm{cr}} \sim 0.4$ K [11], accompanying a residual-entropy release [10, 12]. Although a long-range dipolar interaction would be a key ingredient, full explanation of this transition is still not given yet.

Recently, another type of ice-rule breaking transition has been predicted by Ruff *et al* [13]. This transition occurs in a field slightly tilted away from [112] to the [111] direction. As shown in figure 1, in this situation the directions of spins A, C and D are fixed as indicated. While H is small, spin B, which forms an fcc lattice, points outward due to the ice rule. As H increases, inversion of the spin B occurs to gain the Zeeman energy. Just at the critical field of the spin flip, the internal field acting on spin B from neighbouring spins A, C and D is compensated by the external field and the Ising symmetry of spin B is recovered. Long-range magnetic interactions between spins B then lead to a ferromagnetic ordering. Below the ordering temperature T_{c}, the spin flip becomes a first-order transition. The predicted phase transition near the [112] field has recently been observed by ac susceptibility [14] and dc magnetization [15] measurements. It should be noticed that there is no entropy change associated with this transition, because it is merely an inversion of spins B.

In view of the entropy change involved, the nature of the above two first-order transitions should be different from each other. It is then of interest to examine how the spin-flip transition evolves when H is rotated from [111] towards the [112] direction. In this work, we have studied the ice-rule breaking spin flip in a field rotated in the $(1\bar{1}0)$ plane.

2. Experimental details

A single crystal of $\mathrm{Dy_2Ti_2O_7}$ was prepared by the floating-zone method using an infrared furnace. The crystal was cut into a thin plate of $0.25 \times 2 \times 2\ \mathrm{mm}^3$ (mass of 6.9 mg), in order to

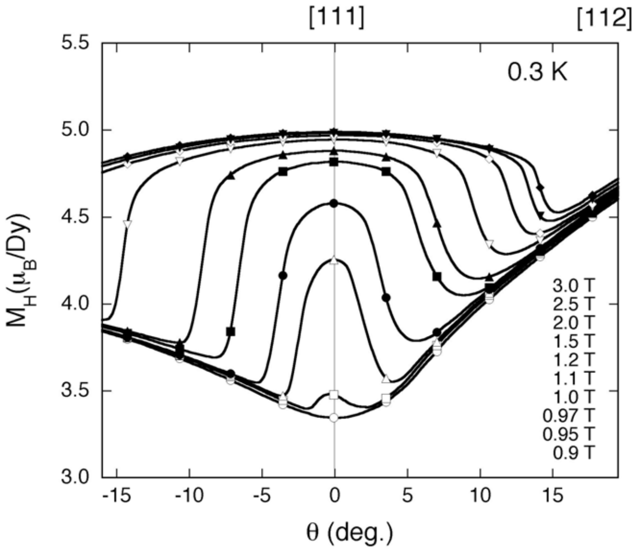

Figure 2. Field-angle variation of the magnetization (M_H) for $Dy_2Ti_2O_7$ obtained at 0.3 K in various fields rotated in the $(1\bar{1}0)$ plane.

achieve a good thermal contact. The largest face was the $(1\bar{1}0)$ plane, along which a magnetic field was applied in order to minimize the demagnetization effect.

Angle-resolved dc magnetization measurements were carried out by a capacitive Faraday method using a ^{3}He refrigerator [15]. Rotating the cryostat using a stepper motor controlled by a computer, the magnetization was measured as a function of the field angle with a resolution of 0.01°. The accuracy of the crystal orientation was within ±0.5°.

3. Results and discussion

In figure 2, we show the field-angle dependence of the magnetization M_H obtained at 0.3 K in various fields between 0.9 T and 3 T, rotated in the $(1\bar{1}0)$ plane. Here M_H denotes the magnetization component parallel to H. The data in figure 2 were obtained by rotating the field from $\theta = -15°$ to 20°. We have also measured M_H by reversing the field rotation from $\theta = 20°$ to $-15°$, but no appreciable difference was observed in the magnetization behaviour. The data points for 0.9 T represent the angular variation of M_H in the two-in, two-out state. For fields above 0.95 T, a jump in M_H can be seen around the [111] direction. This indicates a spin flip into the three-in, one-out state. The angular region of the three-in, one-out state becomes wider as H increases further. We define the critical angle for the spin flip at each field (>1 T) by the midpoint of the jump in $M_H(\theta)$.

Figure 3 shows the differential susceptibility $\mathrm{d}M_H/\mathrm{d}H$ obtained at 0.3 K as a function of H for some selected field angles. Open (solid) symbols denote the data points obtained by increasing (deceasing) fields. No appreciable hysteresis was observed. The peak in $\mathrm{d}M_H/\mathrm{d}H$ corresponds to the spin flip into the three-in, one-out state. At this temperature, the spin flip for the [111] direction is in a first-order transition regime ($T < T_{\mathrm{cr}}$). As H is rotated from [111] towards the [110] direction (figure 3(a)), the peak position monotonically shifts to the higher field side. When H is slightly tilted from [111] towards the [112] direction (figure 3(b)), the sharp peak of $\mathrm{d}M_H/\mathrm{d}H$ associated with the first-order transition rapidly diminishes with a little

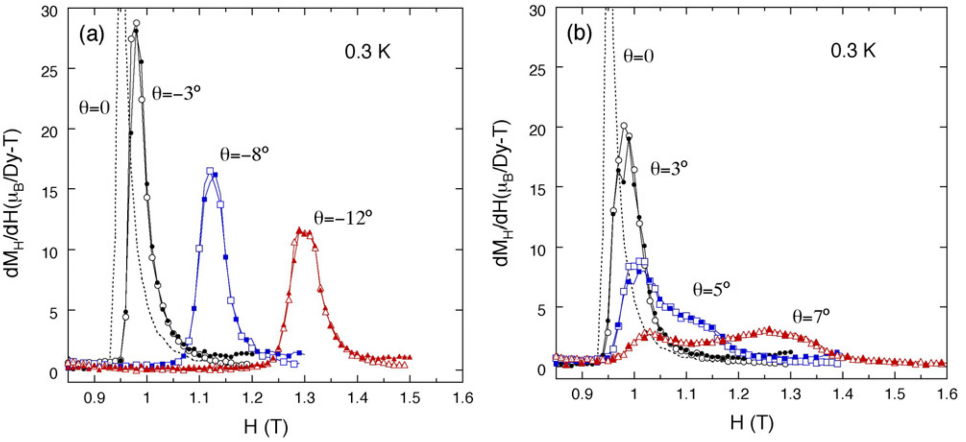

Figure 3. dM/dH near the spin-flip field in $Dy_2Ti_2O_7$ for some selected field directions with $\boldsymbol{H}$ within (a) [110]–[111], and (b) [111]–[112]. The dotted line indicates the data for the [111] direction.

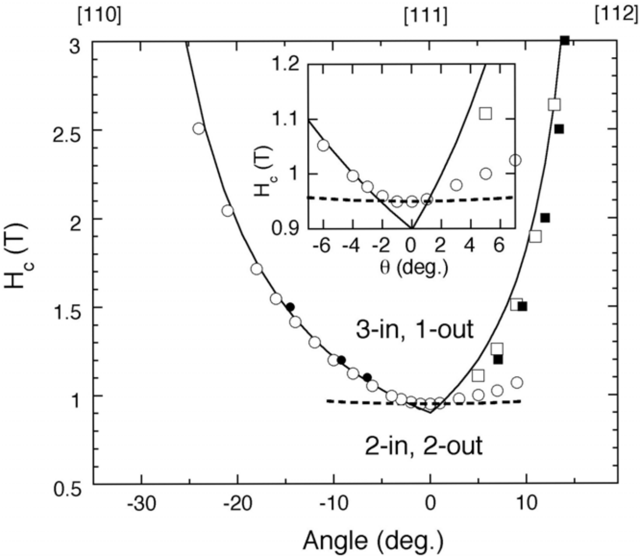

Figure 4. Field-angle dependence of the spin-flip field H_c. Open symbols denote the peak position of the dM/dH plots, whereas solid symbols are the critical angles obtained from the $M_H(\theta)$ data. The solid line is the calculated H_c for a unit tetrahedron on the basis of a nearest-neighbour spin-ice model with $J_{\text{eff}} = 1.01$ K. The dashed line is the angular dependence proportional to $(\cos\theta)^{-1}$. The inset is an enlarged plot around [111].

shift in the position. Interestingly, dM_H/dH for $\theta = 5°$ and $7°$ shows a double peak structure; a new peak appears around 1.1 T and moves to the higher field side as θ increases.

In figure 4, we show the spin-flip field H_c as a function of θ. Open symbols are the data points determined by the dM_H/dH peak, whereas solid symbols are those obtained from the angle variation of the magnetization in figure 2. Interestingly, the $H_c(\theta)$ behaviour is qualitatively asymmetric with respect to the [111] direction; the double-peak feature has been observed in a range 5°–10°. The branch indicated by squares continuously connects to the transition recently observed for H near the [112] direction [14, 15], whereas the branch extending from [111] seems to terminate at $\theta \sim 10°$. This observation clearly demonstrates that the first-order transition observed for [111] is different in origin from the one observed near [112] which is essentially a ferromagnetic ordering of spins on an fcc lattice [13].

The solid line in figure 4 indicates the calculated spin-flip field $H_c(\theta)$ for a unit tetrahedron on the basis of a nearest-neighbour spin-ice model, assuming the moment value of 10 $\mu_B/\mathrm{D}y$:

$$\mu_B H_c = \frac{0.6 J_{\mathrm{eff}}}{\cos\theta + \sqrt{2}\sin\theta}, \qquad (\theta \leqslant 0) \tag{1}$$

$$\mu_B H_c = \frac{0.6 J_{\mathrm{eff}}}{\cos\theta - 2\sqrt{2}\sin\theta}, \qquad (\theta \geqslant 0). \tag{2}$$

For $\theta \geqslant 0$, spin B in figure 1 flips at H_c. When $\theta \leqslant 0$, spin B points inward, but either spin A or spin C points outward in the two-in, two-out state and flips at H_c. In any case, the calculation assumes that the kagomé ice state is completely destroyed when $\theta \neq 0$. The calculated $H_c(\theta)$ has a sharp minimum at $\theta = 0$ ($H \parallel [111]$), and diverges for $\theta = -35.3°$ ([110]) and $\theta = 19.5°$ ([112]) where spins undergoing a flip become normal to the field. The overall angular variation of the H_c data in figure 4 is best reproduced with $J_{\mathrm{eff}} = 1.01$ K. The data points, however, exhibit a marked deviation from (1) and (2) near the [111] direction, as can be seen in the inset of figure 4; the observed critical field shows a rounded minimum at [111]. The dashed line in the figure is the angular dependence proportional to $(\cos\theta)^{-1}$, which is expected when the kagomé ice state is stable against a small deflection of H from [111] and exhibits a collective first-order transition due to long-range interactions; i.e., the [111] component of H drives the transition. Within a narrow range $|\theta| < 2°$, the dashed line fits the data better than the solid line, suggesting the stability of the kagomé ice state. For $\theta < -2°$, the kagomé ice state seems to be destroyed completely and the solid line fits the data points well. For $\theta > 2°$, however, the existence of the branch near the dashed line suggests that a kagomé ice-like disorder partially survives up to 10° and undergoes a collective spin flip. The question is why this asymmetry occurs with respect to the field orientation. This point remains to be clarified in the future.

To summarize, we have studied the ice-rule breaking spin flip in $\mathrm{Dy_2Ti_2O_7}$ in an external field rotated in the $(1\bar{1}0)$ plane and obtained the angle dependence of the spin-flip field $H_c(\theta)$. The overall angular variation of $H_c(\theta)$ can be reproduced by a simple nearest-neighbour spin-ice model, except for the region very close to the [111] direction where a collective first-order phase transition out of the kagomé ice state occurs.

Acknowledgments

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