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LETTER TO THE EDITOR

Ferromagnetic ordering on the triangular lattice in the pyrochlore spin-ice compound $Dy_2Ti_2O_7$

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Abstract

Ice-rule breaking spin-flip in a pyrochlore spin ice compound $Dy_2Ti_2O_7$ has been studied in a field applied near the [112] direction, by means of angle-resolved magnetization measurements. We obtained strong evidence that the magnetization component perpendicular to the $(\bar{1}\bar{1}1)$ kagomé plane undergoes a first-order transition below ∼0.26 K. This transition is driven by a ferromagnetic ordering in the field-decoupled spins on the triangular lattice in $Dy_2Ti_2O_7$, as predicted theoretically.

Frustration among localized spins on some geometrical units such as triangles and tetrahedra can induce novel phenomena. Recently, rare-earth pyrochlore compounds have attracted much interest because spins reside on the vertices of corner-shared tetrahedra [1–6]. In the pyrochlore lattice, a ferromagnetic coupling between the spins leads to full frustration in the case of strong single-ion Ising anisotropy along the ⟨111⟩ axes [4, 7]. Consequently, stable spin configurations for each tetrahedron obey the ice rule: two spins point outward and two spins inward (the so-called 'two-in, two-out' state) in a basic tetrahedron [4]. This is exactly the same rule as the one which hydrogen bonding in water ice obeys, where the two stable positions of a hydrogen atom on each bond correspond to the two states of the Ising spin. As a result, the ground state of the whole spin system is highly degenerate and a static disordered state is formed at low temperature in spite of the structural order of the lattice.

In the typical spin ice compound $Dy_2Ti_2O_7$, a macroscopically degenerate ground state analogous to water ice is realized in zero field below ∼0.5 K [8]. An interesting aspect of the spin ice system is that the ground state degeneracy can be removed by applying a magnetic field [4]. Ramirez *et al* studied the effect of magnetic field on a powdered specimen of $Dy_2Ti_2O_7$ by calorimetric measurements [8]. Interestingly, for fields higher than 1 T, the

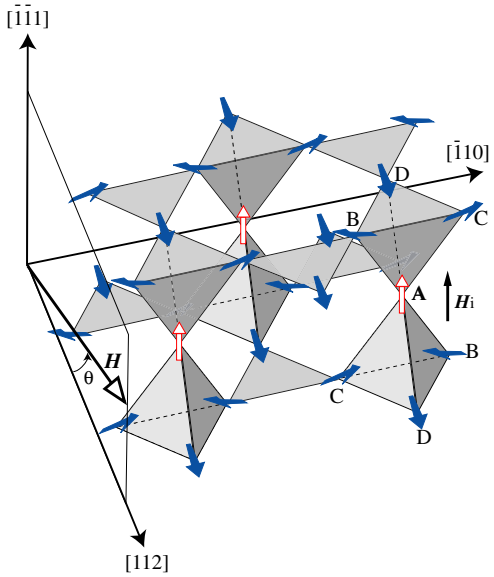

Figure 1. Spin configuration of $Dy_2Ti_2O_7$ in a strong external field $\boldsymbol{H}$ slightly canted away from [112] towards [$\bar{1}\bar{1}$1] directions at an angle θ. Spins on the triangular planes (open arrows), denoted as A, have the Ising axis parallel to the [$\bar{1}\bar{1}$1] direction which is perpendicular to the kagomé and triangular planes. Thick arrows show the spins on the kagomé planes, denoted as B, C and D, which are fully aligned by the field $\boldsymbol{H}$ and induce an internal field $\boldsymbol{H}_i$ on the A sublattice.

(This figure is in colour only in the electronic version)

specific heat data revealed three sharp features at 0.34, 0.47 and 1.12 K, suggesting new phase transitions in magnetic fields.

Later on, field-induced phase transitions in the pyrochlore spin ice were investigated on single crystals by several groups. The anomaly at 1.12 K was ascribed to an ordering in a field applied along the [110] direction of the cubic unit cell [9–11]. Under the [110] field, half of the spins have their Ising axes oriented perpendicular to [110] and are decoupled from the field. These spins behave as unique ferromagnetic Ising spin chains weakly interacting with each other by the long-range dipolar interaction. An intra-chain spin freezing is expected with a rather sharp feature in the specific heat at ∼1.1 K [11]. A long-range ordering is also predicted at ∼1.3 K by recent Monte Carlo simulations [12, 13]. In a [111] field, a new first-order phase transition associated with a collapse of the 'kagomé ice' state has been observed [14–17]. The pyrochlore lattice consists of kagomé and triangular planes stacked alternately along a [111] direction. When a [111] magnetic field is applied, spins on the triangular planes first align along the field direction because they have their Ising axes parallel to [111]. Spin configurations on the kagomé planes are, however, still macroscopically degenerate under the two-in, two-out ice rule. This intermediate state with a finite residual entropy is called 'kagomé ice' [14]. As the field increases further, a first-order transition of liquid-gas type to a fully polarized three-in, one-out state has been observed at ∼0.9 T with the critical end point at ∼0.4 K [16].

Recently, a new phase transition in the triangular lattice has been theoretically discussed by Ruff *et al* [13]. Figure 1 shows the pyrochlore lattice consisting of kagomé and triangular planes stacking along the [$\bar{1}\bar{1}$1] direction. Consider that a strong field ($\boldsymbol{H}$) is applied along the [112] direction within the ($\bar{1}\bar{1}$1) kagomé plane: $\theta = 0$, where θ is the angle between $\boldsymbol{H}$ and the [112] direction. The spins denoted by B, C and D in the kagomé plane then align

along the $[1\bar{1}1]$, $[\bar{1}11]$ and [111] directions, respectively, so as to maximize the Zeeman energy gain. The spin denoted by A on the triangular plane, however, is decoupled from the field because its Ising axis is normal to the field. In this situation, an internal field $\boldsymbol{H}_{\rm i}$ due to the nearest-neighbour interaction with spins B–D forces all the spins on the A sublattice to point along $[\bar{1}\bar{1}1]$ to maintain the two-in, two-out spin configuration on each tetrahedron, as shown in the figure. When the magnetic field is slightly tilted from [112] towards the [111] direction ($\theta < 0$), a field component antiparallel to $[\bar{1}\bar{1}1]$ appears and couples to the spin A. This field component compensates the internal field $\boldsymbol{H}_{\rm i}$ acting on the spin A. If the applied field is strong enough, the complete cancellation of $\boldsymbol{H}_{\rm i}$ can occur at a relatively small critical angle $\theta_{\rm c}$ of the field, and the spins on the triangular lattice are decoupled from spins on the kagomé lattice. One can then except that while the spin configurations in the kagomé planes remain unchanged, a flipping of the spins on the A sublattice towards the $[11\bar{1}]$ direction occurs as the field is further tilted across $\theta_{\rm c}$. Within the nearest-neighbour spin ice model, the field-decoupled spins are not interacting with each other, and the spin-flip at $\theta_{\rm c}$ is not a phase transition. Ruff *et al* [13] pointed out that a ferromagnetic coupling arising from a long-range dipolar interaction, in the presence of a weak antiferromagnetic third nearest-neighbour interaction $J_3 \sim -0.022$ K, led to a ferromagnetic ordering of the field-decoupled spins ($\theta = \theta_{\rm c}$) at $T_{\rm c} \sim 0.35$ K. Below $T_{\rm c}$, the spin-flip at $\theta_{\rm c}$ then becomes a first-order transition.

Very recently, the predicted phase transition near the [112] field has been studied by Higashinaka *et al* by means of ac susceptibility measurements on single crystals of $Dy_2Ti_2O_7$ [18]. They detected the $[11\bar{1}]$ component of the susceptibility by applying ac fields along the $[11\bar{1}]$ direction, under the static fields applied along the [112] and the $[11\bar{1}]$ directions controlled independently by using a vector type magnet. With the $[11\bar{1}]$ field of 0.25 T which just cancelled the internal field from the adjacent kagomé lattice, they obtained a signature of a phase transition in the triangular lattice spins at ∼0.28 K. The observed $[11\bar{1}]$ susceptibility, however, did not show a clear divergence at the critical temperature; they could not conclude solely from their experiment that the phase transition is a ferromagnetic ordering as theoretically predicted. In order to further explore the predicted ferromagnetic transition, we have performed angle-resolved dc magnetization measurements on a single crystal of $Dy_2Ti_2O_7$, and obtained the first thermodynamic evidence for a ferromagnetic transition of field-decoupled spins on the triangular lattice in a field near the [112] direction.

A single crystal of $Dy_2Ti_2O_7$ was grown by the floating-zone method using an infrared furnace. The crystal was cut into a thin plate of $0.25 \times 2 \times 2$ mm^3 (mass of 6.9 mg). 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 magnetization measurements were done by the Faraday method. A sample with a magnetization $\boldsymbol{M}$ was placed at a vertically off-centred position of a split-pair superconducting magnet that produced a horizontal field $\boldsymbol{H} \parallel \hat{x}$. Since there is a finite field gradient $\partial H_x/\partial z$ at the sample position, the sample feels a magnetic force $(\boldsymbol{M} \cdot \hat{\boldsymbol{H}})\partial H_x/\partial z$ along the vertical (z) direction, where $\hat{\boldsymbol{H}}$ is a unit vector parallel to $\boldsymbol{H}$. This force, which is proportional to the magnetization component parallel to $\boldsymbol{H}$, was detected using a force-sensing parallel-plate capacitor. The capacitor, on which the sample was mounted, was cooled by a ^{3}He cryostat down to 0.28 K. 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°. The details of the experimental set-up will be published elsewhere.

In figure 2, we show the field-angle dependence of the magnetization M_H $(=\boldsymbol{M} \cdot \hat{\boldsymbol{H}})$ obtained at temperatures above 0.29 K in a field of 2 T rotated in the $(1\bar{1}0)$ plane. The field strength of 2 T is found to be enough to saturate the spins on the kagomé lattice in the temperature range investigated. The data in figure 2 were obtained by rotating the field

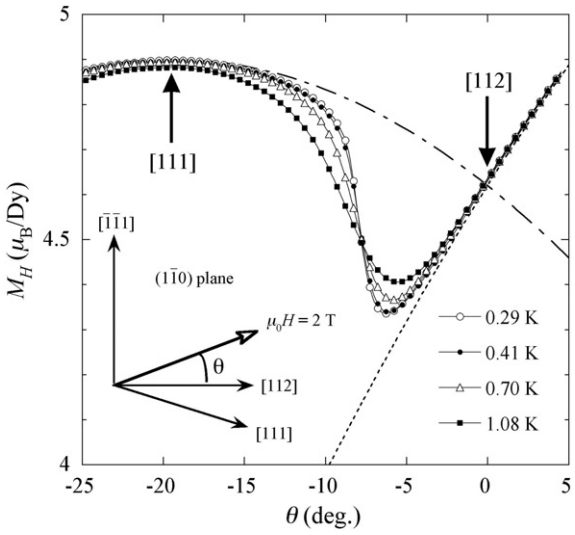

Figure 2. Field-angle variation of the magnetization (M_H) for $Dy_2Ti_2O_7$ obtained at temperatures of 0.29 K, 0.41 K, 0.70 K and 1.08 K in a field of 2 T rotated in the (1$\bar{1}$0) plane. The dotted and the dot–dashed lines represent the field-angle variation of the calculated saturation magnetizations for two-in, two-out and three-in, one-out spin configurations, respectively. The field angle θ is measured with respect to the [112] direction (inset).

from $\theta = 5°$ to $-25°$, passing through the [111] direction ($\theta = -19.4°$). We have also measured by reversing the field rotation from $\theta = -25°$ to 5°, but no appreciable difference was observed in the magnetization behaviour. The dotted and the dot–dashed lines represent the calculated angular dependence of the saturation magnetization for the two-in, two-out and three-in, one-out spin configurations, respectively. Near the [112] direction, the measured magnetization $M_H(\theta)$ follows the angular variation expected for the two-in, two-out structure well. At $\theta = \theta_c \sim -8°$, $M_H(\theta)$ exhibits an abrupt jump to the value expected for the three-in, one-out state, indicating that spin-flip occurs in the triangular lattices as described above. It should be noticed that this magnetization jump at θ_c rapidly becomes sharper with decreasing temperature.

This spin-flip behaviour can be shown more clearly by extracting the magnetization component along the [$\bar{1}\bar{1}$1] direction, parallel to the Ising axis of the triangular lattice. The inset of figure 3 shows the angular relation of the magnetization of the system. $\boldsymbol{M}$ can be expressed as a sum of the kagomé lattice ($\boldsymbol{M}_k$) and the triangular lattice ($\boldsymbol{M}_\triangle$) magnetizations: $\boldsymbol{M} = \boldsymbol{M}_k + \boldsymbol{M}_\triangle$. At low T in a sufficiently high field (>1.5 T) near the [112] direction, $\boldsymbol{M}_k$ is almost saturated and fixed (‖[113]). Let us recall that the measured magnetization $M_H(\theta)$ in figure 2 is a component of $\boldsymbol{M}$ parallel to $\boldsymbol{H}$. Thus, $M_H = \boldsymbol{M} \cdot \hat{\boldsymbol{H}} = M_t \sin\theta + M_{[112]} \cos\theta$, where M_t and $M_{[112]}$ are the transverse ([$\bar{1}\bar{1}$1]) and the in-plane ([112]) components of $\boldsymbol{M}$, respectively, and $\hat{\boldsymbol{H}} = (\cos\theta, \sin\theta)$. Note that only $\boldsymbol{M}_k$ contributes to $M_{[112]}$. Thus, we may assume that $M_{[112]}$ is independent of θ within the present conditions, and $M_{[112]} = M_H(0)$. We thus obtain: $M_t = (M_H(\theta) - M_H(0)\cos\theta)/\sin\theta$. Introducing a transverse component of the field, $H_t = H \sin\theta$, M_t can be expressed as a function of H_t.

In figure 3, we show M_t as a function of H_t^* at various temperatures above 0.29 K. Here H_t^* denotes the transverse field for which a demagnetization field correction is made using a demagnetization factor $N = 0.085$ expected for an oblate ellipsoid with an aspect ratio of ∼8: $H_t^* = H_t - NM_t$ (M_t is in units of A m^{-1}). The dotted and the dot–dashed lines

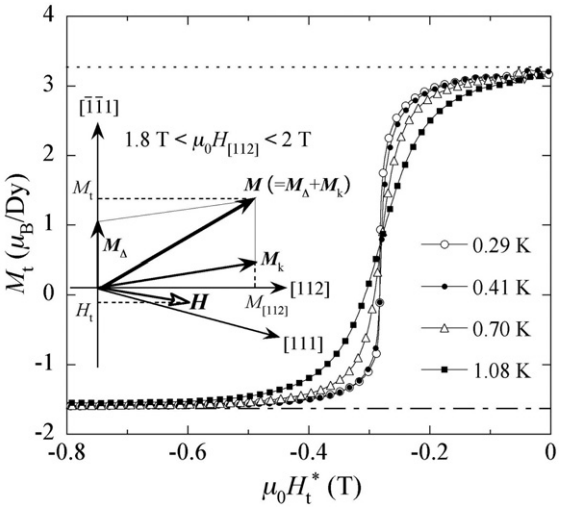

Figure 3. Transverse magnetization M_t versus H_t^* for $Dy_2Ti_2O_7$ with a strong in-plane field along the [112] direction. A demagnetization field correction has been done for the transverse field H_t^*, as described in the text. The in-plane field component $\mu_0 H_{[112]}$ ($=\mu_0 H \cos\theta$) is in the range 1.8–2.0 T in these data ($\mu_0 H = 2$ T). The dotted and the dot–dashed lines represent the calculated saturation magnetizations for two-in, two-out and three-in, one-out spin configurations, respectively. The inset shows the definition of the transverse components of the magnetization and the magnetic field, where $M_\triangle$ and M_k denote the magnetization of the triangular and the kagomé lattices, respectively.

indicate the expected transverse magnetizations for the two-in, two-out and three-in, one-out states, respectively. The data points clearly show a spin-flip from the two-in, two-out state near $\mu_0 H_t^* \sim 0$ to the three-in, one-out state for $\mu_0 H_t^* < -0.4$ T. It should be noticed that M_t has a constant offset of 0.82 μ_B/Dy which comes from the transverse component of the kagomé lattice magnetization M_k. The critical field of the spin-flip is obtained as -0.28 ± 0.02 T. This value is in fair agreement with the estimate of -0.25 T by Higashinaka *et al* [18]. Apart from the offsets in M_t and H_t^*, the behaviour of M_t strongly resembles that of ferromagnetic systems; the spin-flip becomes sharper on cooling, suggesting the divergence of the susceptibility.

In order to examine the critical behaviour of M_t in more detail, we plot in figure 4 the differential susceptibility dM_t/dH_t^* near the spin-flip field. dM_t/dH_t^* exhibits a peak at the spin-flip field. The peak height dramatically increases at low T, implying a rapid narrowing of the spin-flip. The inset shows the reciprocal of the peak height, $(dM_t/dH_t^*)^{-1}_{peak}$, plotted as a function of T. As can be seen from the inset, dM_t/dH_t^* tends to diverge below $T = 0.3$ K. Since no symmetry change is expected (the Ising symmetry is always broken) for spins on the triangular lattice when $H_t^* \neq -H_i$, the spin-flip must turn into a first-order phase transition of liquid-gas type below a critical point T_c. This first-order transition is driven by the ferromagnetic dipolar interaction between the spins on the triangular lattice [13]. Just at $H_t^* = -H_i$, the Ising symmetry is recovered for those spins and a symmetry breaking second-order ferromagnetic ordering occurs at T_c. Since levelling behaviour of dM_t/dH_t^*, which is expected in a ferromagnet for $T < T_c$, has not been observed in this experiment, we expect T_c to be slightly below the present base temperature of 0.29 K. Power-law behaviour $(dM_t/dH_t^*)_{peak} \propto (T - T_c)^{-\gamma}$ was best reproduced in the temperature range 0.31–0.45 K with $T_c = 0.26 \pm 0.01$ K, giving the critical exponent $\gamma = 1.30 \pm 0.05$. Our estimate of T_c is in good agreement with that of Higashinaka *et al* [18], requiring a weak antiferromagnetic

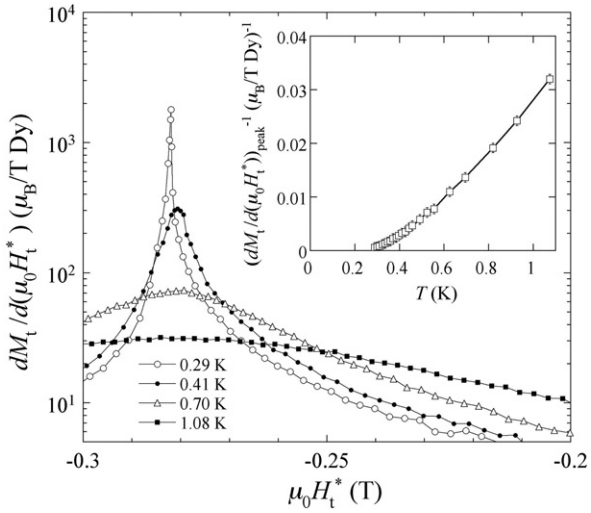

Figure 4. Differential susceptibility dM_t/dH_t^* of $Dy_2Ti_2O_7$ near the spin-flip field. The inset shows the reciprocal of the peak value $(dM_t/dH_t^*)_{peak}$ as a function of temperature. $(dM_t/dH_t^*)_{peak}$ tends to diverge at ∼0.26 K, indicating the existence of a phase transition.

exchange $J_3 \sim -0.028$ K between the spins on the triangular lattice to reduce the transition temperature [13]. It should be noticed that the peak position of dM_t/dH_t^* in figure 4, which corresponds to the compensating field, slightly decreases in magnitude with increasing T. This can be ascribed to a decrease in the internal field H_i due to the thermal excitations of spins in the kagomé lattice, as also pointed out in [13].

It would be of interest to compare the present results with the first-order transition observed in a [111] field for $Dy_2Ti_2O_7$ [16]. There are obvious similarities between these two transitions; both of these are ice-rule breaking, symmetry-sustaining first-order transitions. A careful comparison of these two phenomena, however, reveals some important differences. The first-order spin-flip transition for $T < T_c$ discussed here is merely inversion of spins on the triangular lattice. Thus, no entropy change is involved in the transition, if we forget the minor effect of the thermal excitations of spins in the kagomé lattice. By contrast, the ice-rule breaking first-order transition in a [111] field lifts the macroscopic degeneracy of the kagomé ice state [15, 16] accompanying a substantial decrease of the entropy, as directly confirmed by the magnetocaloric effect measurements [17]. The difference in nature between these transitions is reflected in the thermal variation of the critical fields, as expected from the Clausius–Clapeyron equation; the critical field for the [111] transition shows a rather large *positive shift* of 0.08 T K^{-1} in accordance with the large entropy release [16], whereas that of the transition discussed here seems to show a weak *decrease* in amplitude as described above. It is also noteworthy that the shape of the magnetization curves across the transition in figure 3 is also largely different from that for the [111] transition. The former has a symmetric S-shape as expected for a ferromagnet, whereas the latter is highly asymmetric with a sharp onset and a gradual settling even at temperatures slightly above the critical point, as can be seen in figure 1 of [14]. This observation also indicates a non-trivial change in the spin configuration associated with the [111] transition.

In conclusion, we have studied a theoretically predicted ferromagnetic transition in the spin ice compound $Dy_2Ti_2O_7$ in an external magnetic field near the [112] direction by means of field-angle dependent magnetization measurement. We observed strong evidence of a long-

range ferromagnetic ordering of field-decoupled spins on the triangular planes, confirming the importance of long-range interactions in this compound.

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