Observation of a Liquid-Gas-Type Transition in the Pyrochlore Spin Ice Compound $Dy_2Ti_2O_7$ in a Magnetic Field

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Low temperature magnetization measurements on the pyrochlore spin ice compound $Dy_2Ti_2O_7$ reveal that the ice-rule breaking spin flip, appearing at $H \sim 0.9$ T applied parallel to the [111] direction, turns into a novel first-order transition for $T < 0.36$ K which is most probably of a liquid-gas type. T-linear variation of the critical field observed down to 0.03 K suggests the unusual situation that the entropy release across the transition remains *finite* [~ 0.5 (J/K) · mol-Dy] as $T \to 0$, in accordance with a breaking of the macroscopic degeneracy in the intermediate "kagomé ice" state.

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The pyrochlore oxide $Dy_2Ti_2O_7$ is considered to be a model system of "spin ice" materials, whose magnetic moments obey the same ordering rule as the proton ordering in water ice [1,2]. In this compound, Dy ions are residing on the vertices of corner-linked tetrahedra. Because of a strong single-ion anisotropy, the ground state of Dy^{3+} is well expressed by an Ising doublet with local $\langle 111 \rangle$ quantization axes [3,4]. A ferromagnetic nearest-neighbor interaction then leads to a strong geometrical frustration, preventing the system from long-range ordering [1]. The spins are disordered with local configurations obeying the rule that two spins point outward and two spins inward ("ice rule") in a basic tetrahedron, and the ground state is macroscopically degenerate with a residual entropy very much like the value [1.68 (J/K) · mol] of water ice [5]. The actual ferromagnetic coupling in $Dy_2Ti_2O_7$ is, however, considered to be dipolar in origin, due to the large magnetic moment of Dy [6,7]. Whether the long-range nature of the interaction leads to a true *ordered* ground state or not is an intriguing issue which has not been resolved yet [7–9]. Experimentally, no phase transition is detected in $Dy_2Ti_2O_7$ at zero magnetic field down to 50 mK [10,11].

An interesting aspect of the spin ice system is that the macroscopic degeneracy is broken by application of magnetic fields, and various types of ordered (aligned) states will show up depending on the field directions [7,10,12]. When the field is applied along the [100] direction, the degeneracy is completely broken because all four spins on a basic tetrahedron can uniquely align so that they all have a component of magnetic moment parallel to the field, without breaking the ice rule. The effect of magnetic field is more complex when the field is applied along [111] [12]. For this field direction, the system first magnetizes under the ice rule to a partially aligned state, in which one of the four spins on each tetrahedron has a component of moment antiparallel to the field. As the field becomes strong enough to overcome the magnetic interaction, the ice rule breaks down and a fully ordered "three-spin-in, one-spin-out" state appears. The resulting magnetization curve exhibits a plateau in the intermediate field range followed by a spin flip [11,13,14]. It should be stressed that, as pointed out recently, the intermediate plateau state still has macroscopic degeneracy in the layers of kagomé lattice with residual zero-point entropy ("kagomé ice" state) [14–16].

How the ordered state evolves out of the disordered state by application of magnetic field is an interesting, yet unsettled issue. In a simple case, this would be a continuous process and no phase transition occurs at finite T. Until now, only the Monte Carlo simulations on the nearest-neighbor spin ice model has predicted a first-order transition for $H \parallel [100]$ at temperatures below the critical point $T_{cr} = 0.16J$ [12], where J is a nearest-neighbor ferromagnetic exchange constant. This transition does not involve a change in symmetry and the phase diagram is analogous to that for liquid-gas transitions, which is unprecedented in localized spin systems. However, to explore this transition would be very difficult in $Dy_2Ti_2O_7$ since, as will be shown later, a strong irreversibility due to spin ice freezing starts to develop in the initial magnetization for $T \leq 0.7$ K [17,18], well above T_{cr} [19]. In this Letter, we have examined the degeneracy breaking for the field direction along [111] in $Dy_2Ti_2O_7$ at very low temperatures. We particularly paid attention to the ice-rule breaking spin flip to a fully ordered state. We found that the spin flip is a "fast" process with no hysteresis even at relatively low temperatures down to $\sim$0.4 K and, more importantly, evolves into a symmetry sustaining first-order transition below 0.4 K.

A single crystal of $Dy_2Ti_2O_7$ was prepared by a floating-zone method using an infrared furnace. In order to achieve a good thermal contact and to minimize the demagnetizing field effect, the crystal was cut into a thin plate of dimensions $0.25 \times 2 \times 2$ mm^3, with the [111] direction oriented along the plane [20]. dc magnetization measurements were carried out by capacitive Faraday magnetometers with use of a ^{3}He and dilution

refrigerators [21]. In all the measurements, a field gradient of 3 T/m was applied to the sample. Since strong irreversibility appeared in the initial magnetization curves at $T < 0.7$ K, all the measurements were done after zero-field cooling the sample from above 0.7 K.

In Fig. 1, we show the magnetization curves of $Dy_2Ti_2O_7$ for $H \parallel [111]$ obtained at temperatures above 0.35 K. The result at 1.65 K is in good agreement with the previous measurements done at 1.8 K [11,13] where only a gradual change of the magnetization is observed. On cooling below 1 K, a plateau develops in the magnetization curves at around 0.5 T. The magnetic moment of the plateau is very close to the value 3.33 μ_B/Dy, expected for the partially aligned two-in/two-out state as shown in the inset of Fig. 1. Here, the apical spin on each tetrahedron is aligned to the field direction since its Ising axis is parallel to H and is therefore subject to the largest Zeeman energy. Since the ice rule is maintained in the plateau state, one of the other three spins on the basal plane of the tetrahedron has a component of magnetic moment antiparallel to the field direction, as shown in the inset. The plateau state thus becomes unstable with further increasing field, and a sharp spin flip occurs at ~0.9 T where the Zeeman energy overcomes the magnetic interaction to break the ice rule, in accordance with the results of Monte Carlo simulations [7,11,12]. The moment value above 1.5 T agrees well with the fully saturated value $\sim 5\mu_B$/Dy of the three-spin-in one-spin-out state.

It should be noticed that the initial part of the magnetization curve for $T = 0.35$ K shows a large hysteresis below 0.5 T, as indicated by thin arrows in Fig. 1. This irreversibility disappears on warming the sample above ~0.7 K, and can be ascribed to the slow dynamics of the spin ice [17,18]; the initial magnetization process from the zero-field disordered state involves correlated rotations of magnetically coupled spins under the ice rule, and should have a very slow relaxation time. The situation is the same for the other field directions $H \parallel [100]$ and [110]. Very interestingly, no appreciable hysteresis is found in the ice-rule breaking spin flip around 1 T even for $T = 0.35$ K. This is probably because the spins participating in the flipping are not coupled with each other by the nearest-neighbor interaction. Roughly speaking, the spin flip is a "single site" phenomenon if we forget the long-range part of interactions, and could be a fast process. However, this does not mean that the interactions are unimportant, as will be shown in the following.

In Fig. 2, we show some results of the differential susceptibility dM/dH of $Dy_2Ti_2O_7$ near the spin-flip field where dM/dH peaks. The peak height, denoted as $(dM/dH)_{peak}$, dramatically increases at low T, implying a rapid narrowing of the spin flip. If the spin flip is a single-site phenomenon in which the spins undergoing the flip simply feel the effective field which is a sum of the external field and the fixed molecular fields from the surrounding frozen spins, the width of the magnetization jump would be proportional to T and therefore

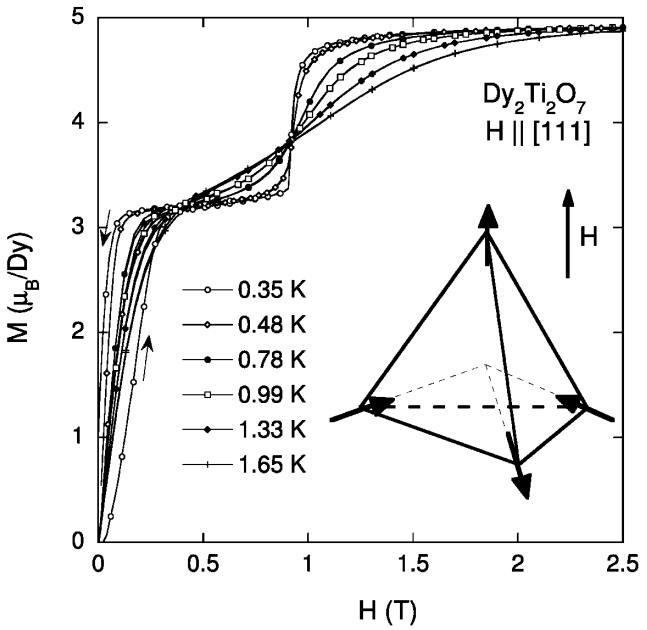

FIG. 1. Magnetization curves of $Dy_2Ti_2O_7$ for $H \parallel [111]$, obtained at various temperatures above 0.35 K. Magnetization data were acquired at an interval of 0.02 T for both increasing and decreasing field sweeps. The thin arrows along the magnetization curve for $T = 0.35$ K indicate a hysteresis in the initial magnetization process below 0.5 T. The inset shows an example of the two-in/two-out spin configurations in the plateau state, where one of the spins on the basal triangle has a component of magnetic moment antiparallel to H.

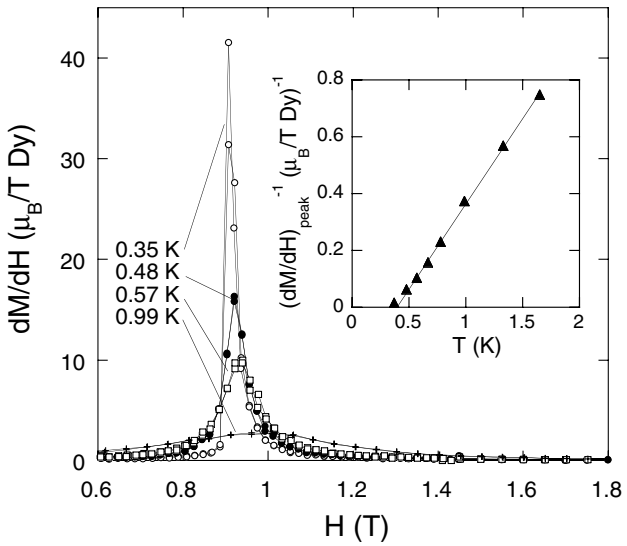

FIG. 2. Differential susceptibility dM/dH of $Dy_2Ti_2O_7$ for $H \parallel [111]$ near the spin-flip field. The inset shows the reciprocal of the peak value $(dM/dH)_{peak}$ as a function of temperature. $(dM/dH)_{peak}$ tends to diverge at around 0.4 K, suggesting that the system undergoes a cooperative phase transition. The solid line is a guide to the eyes.

$(dM/dH)_{\text{peak}}$ is expected to diverge as T^{-1}. However, this is not the case in $Dy_2Ti_2O_7$. The inset of Fig. 2 is a reciprocal of $(dM/dH)_{\text{peak}}$ plotted as a function of T. Very interestingly, $(dM/dH)_{\text{peak}}$ tends to diverge at a finite temperature just below 0.4 K. This fact implies the importance of magnetic correlation, and strongly suggests a new phase transition. A simple linear extrapolation of the $(dM/dH)^{-1}_{\text{peak}}$ plot gives the onset of the transition to be ~0.38 K.

In order to further explore the nature of this new phase transition, we extended the measurements to still lower temperatures using a dilution refrigerator and some of the results below 0.37 K are shown in Fig. 3. The spin flip at low temperatures is characterized by an abrupt onset at ~0.9 T and a gradual settling at higher fields. The latter feature, the rounding of the step at the higher field side, does not change much on further cooling to 0.05 K, implying that thermal excitations are not the origin. This fact also indicates that the spin flip is by no means a simple single-site effect, and points to the relevance of long-range interactions. Very importantly, we observed a small hysteresis in the transition field for $T = 0.19$ K and 0.05 K as indicated by arrows in the inset of Fig. 3. From these results, we conclude that the system undergoes a first-order phase transition to the fully ordered state.

In Fig. 4, we show the temperature variation of the transition field defined by the peak position in dM/dH. The data in Fig. 4 were taken at a different run, with the sample remounted on the magnetometer [22]. Here, the solid circles (squares) denote the transition fields obtained at the increasing (decreasing) field sweeps. At the base temperature of 30 mK, the hysteresis of the transition amounts to ~0.04 T. The hysteresis continuously decreases on warming and seems to disappear around 0.34 K which gives a lower bound for the critical point where the first-order transition terminates, consistent with the divergence of $(dM/dH)_{\text{peak}}$ at ~0.38 K. We therefore conclude that the first-order critical point T_{cr} exists at $T_{\text{cr}} = 0.36 \pm 0.02$ K. We define the critical field of the transition H_{c} by taking average of the increasing and the decreasing field data, and the result is given by open triangles in Fig. 4. The first-order transition line $H_{\text{c}}(T)$ shows a nearly linear shift to a lower field side with decreasing T below T_{cr}. We found no evidence of any other transition line to branch from the critical point. There is thus a way to convert the system from the plateau state to the aligned state *continuously* by avoiding the critical line, implying that there should be no symmetry change across the transition [23]. The $H_{\text{c}}(T)$ behavior in Fig. 4 is thus analogous to the pressure-temperature phase diagram of a liquid-gas transition, similar to the one predicted for the [100] direction [12]. To the best of our knowledge, this type of nontrivial liquid-gas transition has not been observed previously in localized spin systems [24].

On a first-order critical line, the following Clausius-Clapeyron equation holds:

$$\frac{dH_{\text{c}}}{dT} = -\frac{\Delta S}{\Delta M}, \tag{1}$$

where ΔS and ΔM denote the discontinuities in the entropy and the magnetization across the first-order

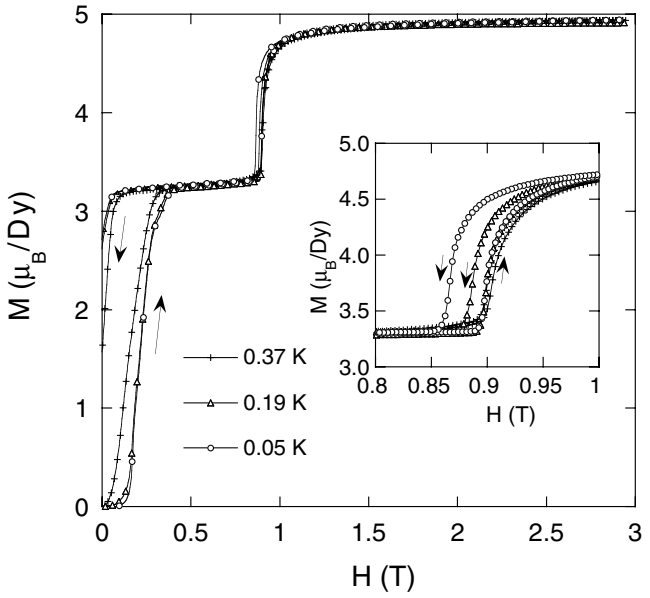

FIG. 3. Magnetization curves of $Dy_2Ti_2O_7$ for $H \parallel [111]$, measured at temperatures down to 0.05 K. The inset shows expanded plots near the critical field. On cooling below 0.37 K, an appreciable hysteresis develops in the transition.

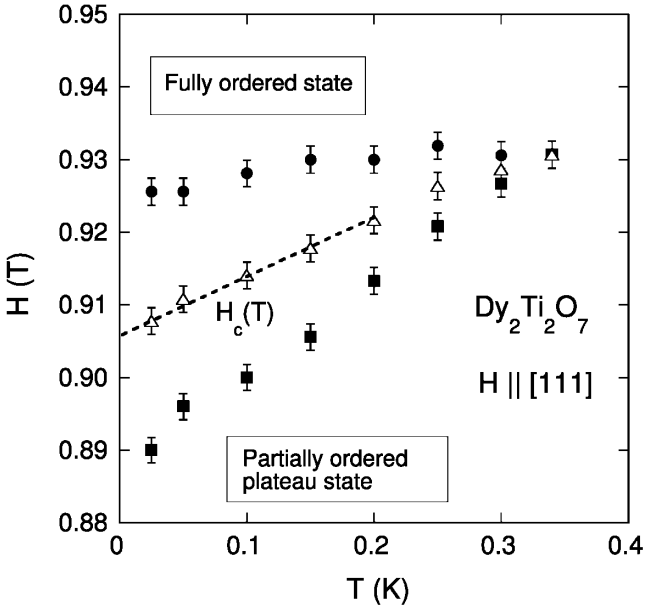

FIG. 4. Thermal variation of the transition field of $Dy_2Ti_2O_7$ for $H \parallel [111]$. Solid circles (squares) denote the data points obtained for increasing (decreasing) field sweeps. Open triangles are the averaged critical field H_{c}, which show a nearly linear temperature variation with $dH_{\text{c}}/dT = 0.08$ T/K (dashed line) at low temperatures.

transition, respectively. Normally, dH_c/dT should tend toward zero as $T \to 0$, since S vanishes at $T = 0$ irrespective of H in ordinary systems. In the present system, however, $H_c(T)$ continues to decrease almost linearly on cooling below T_{cr} without showing a tendency of leveling off. This behavior suggests an unusual situation that the first-order transition accompanies a finite entropy release ($\Delta S < 0$) as $T \to 0$. ΔS can in fact be evaluated by (1). From Fig. 4, dH_c/dT is estimated to be 0.08 T/K (the dashed line in Fig. 4). ΔM has some uncertainty because of the rounding of the magnetization jump at the higher field side (Fig. 3), but we may say that ΔM is in the range $1 \pm 0.3\mu_B$/Dy. ΔS can then be obtained as -0.5 ± 0.15 (J/K) · mol-Dy.

We consider that the finite $\Delta S < 0$ as $T \to 0$ is a direct consequence of the frustration of the system, giving another piece of strong evidence for the zero-point entropy in the plateau state. In the plateau state, the apical spins of the tetrahedra whose Ising axis is parallel to H point to the field direction, but the other spins which form the two dimensional kagomé lattice perpendicular to [111] are still frustrated because the ice rule is preserved. Focusing on the kagomé lattice which is composed of corner-linked triangles, the frustration can be expressed by a modified ice rule that two spins point inward and one spin points outward in a basic triangle. The ground state is then macroscopically degenerate ("kagomé ice" state [14]), with a residual entropy whose exact value has recently been solved by Udagawa *et al.* to be 0.672 (J/K) · mol-Dy [16]. Experimentally, the residual entropy of the plateau state has been estimated by specific heat measurements as 0.8 ± 0.1 (J/K) · mol-Dy by Matsuhira *et al.* [14], and 0.44 ± 0.08 (J/K) · mol-Dy by Higashinaka *et al.* [15]. Our magnetization data indicate that most of the residual entropy is released upon the first-order transition.

In conclusion, we observed a novel field-induced first-order phase transition in the spin ice compound $Dy_2Ti_2O_7$ with magnetic field parallel to the [111] direction. The transition simultaneously breaks the ice rule and the macroscopic degeneracy in the partially ordered spin ice state. The obtained phase diagram is analogous to that for liquid-gas transitions, with unusual temperature variation of the critical field which appears to violate the thermodynamic principle that the entropy change ΔS vanishes as $T \to 0$. While the results share similarity with what has been predicted for a nearest-neighbor spin ice model for $H \parallel [100]$ [12], our results suggest relevance of long-range dipolar interactions to the occurrence of the first-order transition, which are not included in the previous simulations.

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[19] Since the effective nearest ferromagnetic interaction is estimated to be ~1.1 K [6], T_{cr} becomes ~0.18 K.
[20] At low temperatures, the magnetization is so large that we further made a demagnetizing field correction using a demagnetizing factor of ~0.08 obtained for an oblate ellipsoid with the aspect ratio of 8 [R. M. Bozorth, *Ferromagnetism* (D. van Nostrand Co., New York, 1951)]. The basic features of the present data are, however, free from this correction.
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[22] We found that H_c strongly depends on the field orientation and increases when H is tilted from the [111] direction. Because of unavoidable misalignment of the sample, H_c shown in Fig. 4 is slightly higher than those data in Fig. 3.
[23] A phase transition that does not involve a symmetry change should always be of first order. In a magnetic system, the magnetization then becomes discontinuous and the differential susceptibility diverges as the critical point is approached from above [M. E. Fisher and A. N. Berker, Phys. Rev. B **26**, 2507 (1982)].
[24] Ising ferromagnet is known to show a phase diagram of liquid-gas type, with a line of the first-order transition along the $H = 0$ line. In that case the analogy is purely on symmetry, and no latent heat is expected across the first-order transition because the phase boundary is parallel to the temperature axis.