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LETTER TO THE EDITOR

A new macroscopically degenerate ground state in the spin ice compound $Dy_2Ti_2O_7$ under a magnetic field

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Abstract
The low-temperature magnetic properties of the pyrochlore compound $Dy_2Ti_2O_7$ in magnetic fields applied along the [111] direction are reported. Below 1 K, a clear plateau has been observed in the magnetization process in the field range 2–9 kOe, followed by a sharp moment jump at around 10 kOe that corresponds to a breaking of the spin ice state. We found that the plateau state is disordered, with a residual entropy of nearly half the value for the zero-field state, whose macroscopic degeneracy comes from a frustration of the spins on the Kagomé layers perpendicular to the magnetic field.

Geometrical frustration can lead to novel phenomena, such as a macroscopic degeneracy in the ground state with no long-range ordering. Recently, pyrochlore oxides have been attracting much interest because the structure, including corner-shared tetrahedra whose vertices are occupied by spins (figure 1(a)), may show a strong frustration [1–8]. In the pyrochlore lattice, even a ferromagnetic coupling between spins can lead to frustration [4, 8, 9] when there is a strong single-site anisotropy along the local $\langle 111 \rangle$ axes. $Dy_2Ti_2O_7$ is a typical example of such a case, where the ferromagnetic interaction stabilizes the local spin arrangement of two spins pointing outward and two spins inwards (the so-called 'two-in–two-out' state) in a basic tetrahedron (figure 1(a)). For every tetrahedron, there are six possible combinations of spins under the two-in–two-out rule reflecting the global cubic symmetry. Because the ground state is highly degenerate, a static disordered state (the so-called 'spin ice' state) is formed below 1 K in spite of the structural order of the system. In fact, $Dy_2Ti_2O_7$ is found to show a residual ground state entropy of 1.68 J mol^{-1} K^{-1}, which is numerically in agreement with the Pauling entropy for water ice [10, 11].

The spin ice state is closely related to the high symmetry of the pyrochlore structure. Novel features might therefore be expected in the Ising pyrochlore ferromagnet when the degeneracy is partially or totally reduced. Applying a magnetic field is of interest and is the easiest way

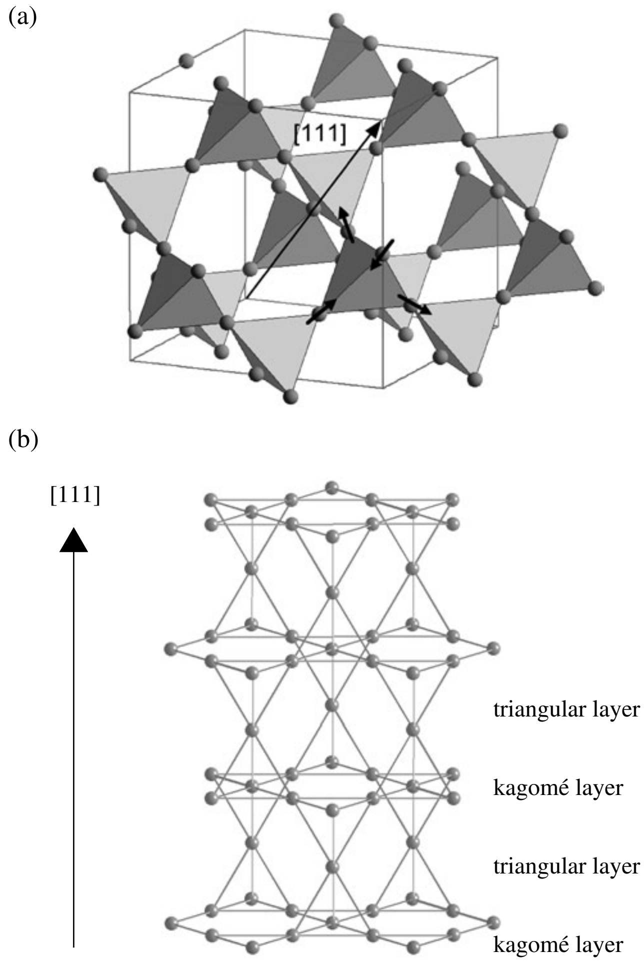

Figure 1. (a) The pyrochlore lattice of corner-sharing tetrahedra whose vertices are occupied by Ising spins of Dy ions. The long arrow shows the [111] direction along which the magnetic field is applied. One of the six two-in–two-out configurations is shown by short arrows. Each spin lies along the axis joining the vertex and the centre of the tetrahedron, due to a strong single-site anisotropy. (b) The pyrochlore lattice viewed along the [111] direction. It consists of an alternating stacking of Kagomé and triangular layers.

to lower the symmetry, and new types of phase transition are predicted, depending on the field direction [12]. In this letter, we report the magnetic properties of the pyrochlore compound $Dy_2Ti_2O_7$ in magnetic fields applied along the [111] direction. The pyrochlore lattice can be viewed as an alternating stacking of Kagomé layers and sparse triangular layers, both of which are perpendicular to the [111] direction (figure 1(b)). By applying a magnetic field along the [111] direction, we found a new macroscopically degenerate state in which, although the magnetization is induced, a macroscopic degeneracy remains in the spin configuration on the Kagomé layers.

Single crystals of $Dy_2Ti_2O_7$ were prepared by the floating-zone method using an infrared furnace equipped with four halogen lamps and elliptical mirrors. The crystals were grown under O_2 gas flow to avoid oxygen deficiency. The typical growth rate was 4 mm h^{-1}.

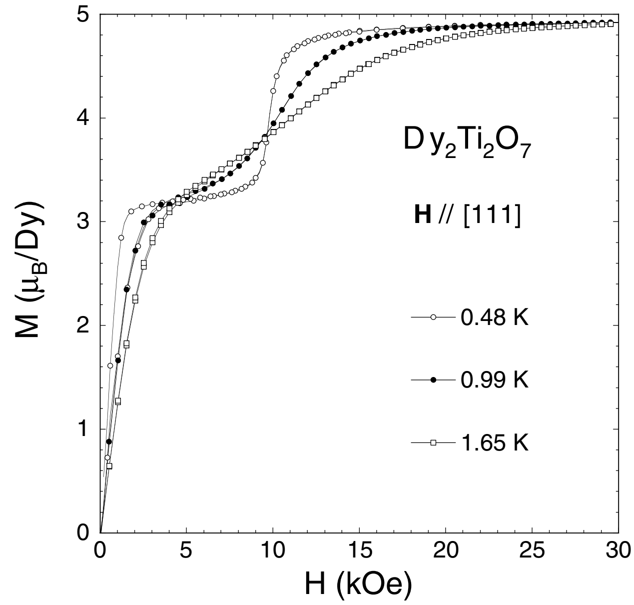

Figure 2. The process of magnetization of $Dy_2Ti_2O_7$ along the [111] direction.

The single crystals obtained were translucent yellow. DC magnetization measurements were made using a capacitive Faraday magnetometer installed in a ^{3}He cryostat, with a field gradient of 300 Oe cm^{-1} [13]. Specific heat measurements were carried out by a relaxation method (PPMS, Quantum Design) down to 0.4 K. The typical sizes of the samples used for the magnetization and specific heat measurements were $0.5 \times 2 \times 2$ and $0.1 \times 1 \times 1$ mm^3, respectively. In order to minimize the demagnetizing field effect, the [111] direction was oriented along the sample plane.

DC magnetization curves of $Dy_2Ti_2O_7$ with magnetic field applied along the [111] direction are shown in figure 2. At $T = 1.65$ K, the magnetization is a gradual function of field with a weak feature at around 10 kOe, and saturates at higher fields to the value $\sim 5\ \mu_B$/Dy. This moment value corresponds to the fully saturated one-in–three-out (or three-in–one-out) state of the Ising pyrochlore lattice with the local Ising axis pointing along the $\langle 111 \rangle$ directions. The result at 1.65 K is in good agreement with the previous measurements made at 1.8 K by Fukazawa *et al* [14].

On cooling below 1 K, the feature at $\sim$10 kOe becomes sharper, and eventually turns into a metamagnetic step at $T = 0.48$ K with a preceding magnetization plateau below $\sim$9 kOe. The magnetic moment of the plateau is very close to the value 3.33 μ_B/Dy, as expected for the saturated moment along the [111] direction, without destroying the ice rule (two-in–two-out state). In fact, the emergence of the plateau is closely associated with the formation of the spin ice state which is evidenced by the appearance of magnetization hysteresis below 5 kOe [7]. Clearly, the metamagnetic step near 10 kOe corresponds to a breaking of the spin ice state by a magnetic field strong enough to overcome the magnetic interactions. This phenomenon has been predicted by Monte Carlo simulations of spin ice models [12, 14, 15], but experimentally only a broad feature had been observed in the previous measurements done at 1.8 K [14]. Our data are the first results in the low-temperature regime where the ice rule configuration is well developed. Magnetization measurements at still lower temperatures are in progress and the results will be published soon [16].

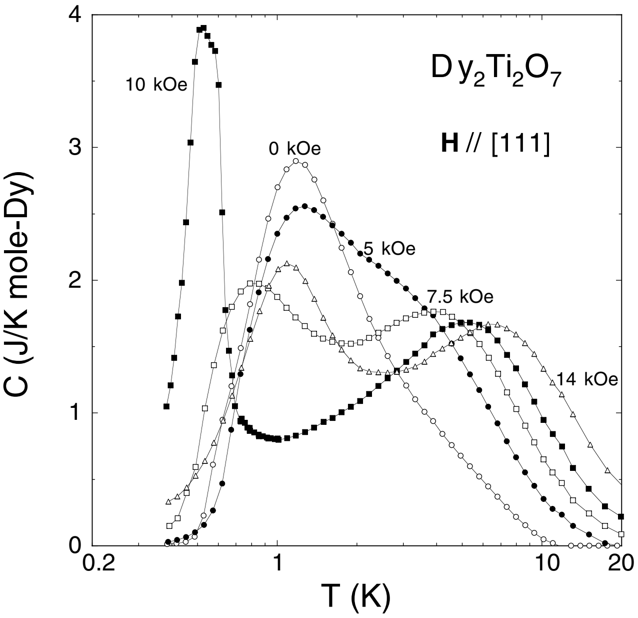

Figure 3. The temperature dependence of the magnetic specific heat C of $Dy_2Ti_2O_7$ measured at various magnetic fields applied along the [111] direction.

In the plateau state, each spin on the triangular layers is considered to be aligned, since its Ising axis is parallel to the field, rendering the Zeeman energy the largest. The remaining spins on the Kagomé layers, however, can only be partially ordered, because the ice rule is maintained. This suggests a new macroscopically degenerate state in this intermediate field range, as will be confirmed by the specific heat measurements.

We were able to fit the raw data taken at zero field in the temperature range between 12 and 19 K to a conventional form for lattice contribution $C = \alpha T^3$ with $\alpha = 4.85 \times 10^{-4}$ J K^{-4}/(mol Dy), which suggests that the magnetic contribution is almost absent there. Assuming that this lattice contribution is independent of magnetic field, the magnetic specific heat at low temperature, below 15 K, was obtained by subtracting it from the raw data. On the other hand, the magnetic specific heat at higher temperature was estimated by subtracting the zero-field data as a lattice part. However, this estimate may suffer from increasing experimental error with increasing temperature, because the lattice part becomes dominant. In figure 3, we show the temperature dependence of the magnetic specific heat $C(T)$ of $Dy_2Ti_2O_7$ under various fields applied along the [111] direction. At zero field, $C(T)$ shows a broad maximum at 1.2 K which is presumably related to a process of freezing to the highly degenerate spin ice state. On applying a magnetic field of 5 kOe, $C(T)$ shows not only a broad maximum at 1.2 K but also a shoulder at 3 K. These features of $C(T)$ split into two broad peaks at the field of 7.5 kOe. The higher-temperature peak at $\sim$4 K shifts still further to the higher-temperature side with further increasing field. This peak probably arises from the Schottky anomaly of Zeeman-split spins on the triangular layers, which are parallel to the field direction and become more stabilized with increasing fields.

On the other hand, the origin of the lower-temperature peak in $C(T)$, which may come from the spins on the Kagomé layer, seems to be more complicated. These spins have a component of the magnetic moment along the [111] field direction that is a third smaller than that on the triangular layers and are therefore subjected to a smaller Zeeman energy. Interestingly, this broad peak shifts to the lower-temperature side with increasing field up to 10 kOe. This fact implies that the lower-temperature peak arises from certain short-ranged magnetic correlations in the Kagomé layer, which must have a close relation to the plateau state observed in the magnetization. The peak becomes very sharp at around 10 kOe and shifts again to the higher-temperature side with further increasing field. In the strong-magnetic-field regime above 10 kOe, we observe two broad peaks in $C(T)$ moving towards the high-temperature side, both of which are ascribed to Schottky-type anomalies arising from the two types of spin on the Kagomé and the triangular layers with different Zeeman splittings.

In order to explore the nature of the plateau state further, we estimated the field variation of the magnetic entropy $S(T)$ by integrating C/T in magnetic fields. We make the assumption that $S(T)$ approaches the value $R \ln 2$ expected for a Kramers doublet of the Dy ions, where R is the gas constant, at temperatures much higher than those for the ground state manifolds but still lower than the range where the crystal-field-split higher levels are populated. As can be seen from figure 3, the zero-field $C(T)$ value above 10 K falls off to nearly zero, indicating that the populations of the excited levels are negligible in this temperature range. We can thus estimate the absolute entropy value at various fields. Figure 4 shows the field dependence of the magnetic entropy $S(H)$ estimated at 0.4 K. Since the zero-field $C(T)$ has already died out at this temperature, the $S(H = 0)$ value of $\sim$1.6 J/(mol Dy) at 0.4 K would be a good estimate of the ground state entropy. This value is very close to the residual magnetic entropy of the spin ice state ($R(1/2)\ln(3/2) = 1.68$ J K^{-1} mol^{-1}), and confirms that the system is in the macroscopically degenerate state at zero field. This residual entropy is partially released by applying a magnetic field of 2 kOe, because the sixfold-degenerate states of the basic tetrahedron become energetically inequivalent. However, the magnetic entropy at 0.4 K still retains a finite value of 0.8 ± 0.1 J K^{-1}/(mol Dy) in the field range of 2.5–7.5 kOe where the magnetization plateau is observed. Because the $C(T)$ value at 5 kOe drops by almost two orders of magnitude on cooling below 1–0.4 K, further entropy release is unlikely to occur below 0.4 K. Therefore, we conclude that the plateau state has a residual ground state entropy of 0.8 ± 0.1 J K^{-1}/(mol Dy).

The specific heat data indicate that the $C(T)$ value at 10 kOe becomes very large at 0.4 K, implying that a rather steep entropy release should occur in this field region, as can be expected for the breaking of the ice rule by the magnetic field. This feature can be seen in figure 4 as a weak step in the $S(H)$ value at around 10 kOe. At fields well above 15 kOe, the spin configuration in the tetrahedron is the unique one-in–three-out state. The system should have no residual ground state entropy at all. In our estimate, however, $S(H)$ above 15 kOe still remains finite up to the value of $\sim$0.4 J K^{-1}/(mol Dy). The reason for this offset might be that the Schottky peak of $C(T)$ above 16 kOe has a long tail to the higher-T side far above 20 K; the experimental error would then be increased by the integration of C/T towards the higher-temperature range and we are probably underestimating the entropy change above 20 K. More precise measurements would be needed to clarify this point.

Let us discuss the spin configuration in the magnetization plateau state. The magnetic field along the [111] direction reduces the sixfold-degenerate two-in–two-out configurations in the basic tetrahedron to threefold-degenerate ones. In this state, every spin on the triangular layer is oriented along the [111] direction whereas the spins on the Kagomé layer are still frustrated because the two-in–two-out ice rule is maintained in each tetrahedron. The Kagomé layer consists of corner-shared triangles (see figure 1(b)) and, under the ice rule, there are two types of triangle having either the one-in–two-out spin configuration or the two-in–one-out one. For each type, there are three ways to align the spins, as shown in figure 5. Here a, b and c indicate the spin configurations of one-in–two-out states in the triangles pointing downward, whereas

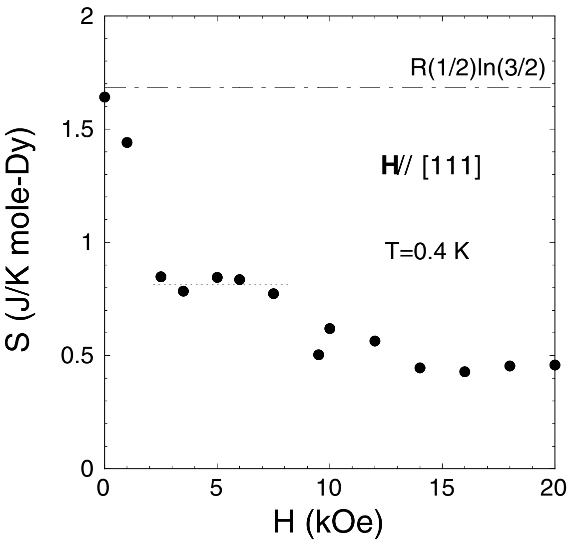

Figure 4. The magnetic field dependence of the magnetic entropy $S(H)$ at 0.4 K. The dashed–dotted line shows a residual ground state entropy of spin ice ($R(1/2)\ln(3/2)$). $S(H)$ shows a plateau (broken line) in the magnetic field range of 3.5–7 kOe.

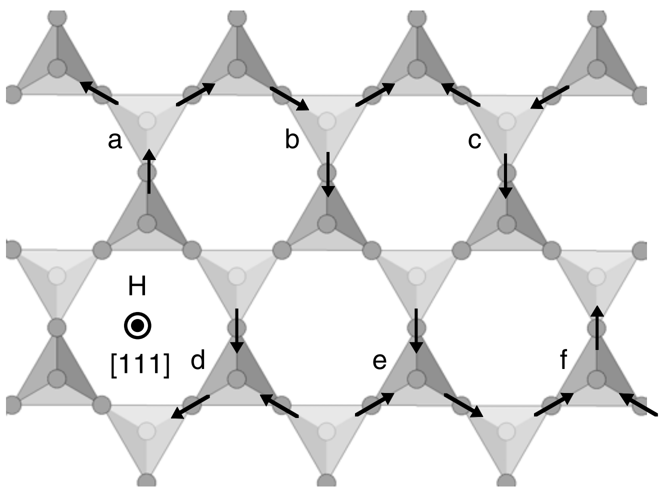

Figure 5. Macroscopic degeneracy in the plateau state (Kagomé ice). a, b and c label the three patterns for the one-in–two-out configurations for triangles with other apical spins above, whereas d, e and f label those for two-in–one-out arrangements for the other triangles with other apical spins below in the Kagomé layer.

d, e and f indicate those of the two-in–one-out states in the upward triangles. Clearly, the plateau state is frustrated and may have a residual entropy, which was recently calculated to be about 40% of the zero-field spin ice state [17], in reasonably good agreement with the results in figure 4. Our experimental data on the magnetization and the specific heat measurements thus confirm this new macroscopically degenerate state: the 'Kagomé ice' state in $Dy_2Ti_2O_7$ under a magnetic field.

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