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A Kagome ice state in the spin ice compound $Dy_2Ti_2O_7$

Ryuji Higashinaka[1], **Hideto Fukazawa**[1,3], **Kazuhiko Deguchi**[1] **and Yoshiteru Maeno**[1,2]

[1] Department of Physics, Kyoto University, Kyoto 602-8502, Japan
[2] International Innovation Centre, Kyoto University, Kyoto 602-8501, Japan

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Abstract

We report on the specific heat and the entropy of single crystals of the spin ice compound $Dy_2Ti_2O_7$ down to 100 mK under magnetic fields along the [111] direction in order to study detailed low temperature properties of the Kagome ice state. Previously, we reported anisotropic release of the residual entropy reflecting the Ising anisotropy. We pointed out that the anisotropic behaviour can be viewed as the difference in frustration dimensionality. In an intermediate field, the entropy for the [111] field direction is different from those of the other principal directions. This is because the frustration structure changes from that of a three-dimensional (3D) pyrochlore to that of a two-dimensional (2D) Kagome lattice with constraint from the ice rule, accompanied by a different zero-point entropy value. We call this state 'the Kagome ice state'. In the Kagome ice state, the value of the residual entropy, $\Delta S_{\mathrm{Kagome}}$, is estimated as 0.598 J K^{-1}/(mol Dy) by Pauling's method.

In the present experiment, we observed that the specific heat at 1 T exhibits a sharp peak at 400 mK and an anomalous upturn at lower temperature. This peak indicates the entropy release from a 1-in 3-out state with no residual entropy to a 1-in 3-free state.

Geometrically frustrated systems exhibit various unusual phenomena: spin ice [1], quantum spin liquid, the anomalous Hall effect etc. Among such compounds, pyrochlore oxides $A_2B_2O_7$ attract a great deal of attention because they have a relatively rare three-dimensional (3D) frustration structure and a large variety of compounds in this class are available.

The spin ice behaviour has been observed in $Ho_2Ti_2O_7$ [1–3], $Dy_2Ti_2O_7$ [1, 4–8] and $Ho_2Sn_2O_7$ [9]. Since there is no long range magnetic ordering of the rare-earth moments in these materials at least down to 50 mK [1, 5], the ground state is believed to be macroscopically degenerate. In fact, the observed residual entropy [4, 10] shows an excellent agreement with the expected zero-point entropy of $(1/2)R\ln(3/2)$ [11].

[3] Present address: Graduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan.

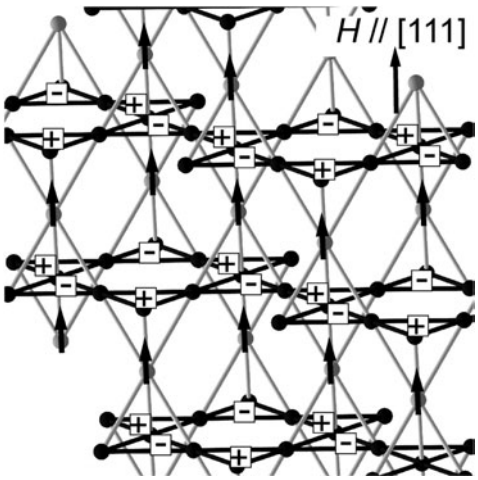

Figure 1. The spin configuration in the Kagome ice state. Plus and minus signs represent that the net moment of the three spins constituting a triangle is positive and negative, respectively, by the ice rule along the field direction [111].

In these materials, the A-site ions constitute a three-dimensional network of corner-shared tetrahedra (the pyrochlore lattice). Because of the crystal field effect, the magnetic moments of the A-site ions, such as Dy^{3+} and Ho^{3+}, have Ising anisotropy along the local $\langle 111 \rangle$ direction, which points to the centre of each tetrahedron from a vertex. Owing to this Ising anisotropy, the spin responses depend on the directions of magnetic fields: the process of release of the residual zero-point entropy should be qualitatively different, reflecting the anisotropic structure of frustration.

In this paper, we report on the specific heat and the entropy of single-crystalline $Dy_2Ti_2O_7$ in magnetic fields along the [111] direction down to 100 mK. To the best of our knowledge, the specific heat below 350 mK in the Kagome ice state has not been reported. We observed a sharp peak at 400 mK and an anomalous upturn below 300 mK at 1 T in the specific heat. We will discuss the relation between the anomalous upturn at 1 T and the Kagome ice state.

The single crystals of $Dy_2Ti_2O_7$ used in this work were grown by a floating zone method [5]. We measured the specific heat between 0.1 and 3 K by a relaxation method using a home-made calorimeter with a dilution refrigerator (Oxford Instrument model Kelvinox25). The sample size was approximately $2.0 \times 2.0 \times 0.06$ mm^3 and the mass was about 1.7 mg. The [111] direction lies on the surface of the plate-like sample.

In the [111] field direction, one of the four Ising spins is parallel to the field and most effectively stabilized by the external field (figure 1). For the other three spins, the nearest-neighbour dipolar interaction dictating the ice rule competes with the Zeeman energy due to the external field: in lower fields, the dominant dipolar interactions stabilize the 2-in 2-out configuration (two spins pointing inward and two spins outward); in higher fields, however, the gain of the Zeeman energy exceeds that of the dipolar interaction and this energy gain stabilizes the 1-in 3-out configuration. This crossover process has been quantitatively confirmed by magnetization measurements [5, 12].

In the 2-in 2-out state, there are three frustrating spins for each tetrahedron and these spins constitute a Kagome lattice. Viewed from the [111] direction, the pyrochlore lattice consists of a layered stacking of a triangular lattice and the Kagome lattice (a pyrochlore slab). The frustration on a 3D pyrochlore changes to that on a 2D Kagome lattice. The ground state of an ordinary Kagome lattice has greater residual entropy than that of a pyrochlore

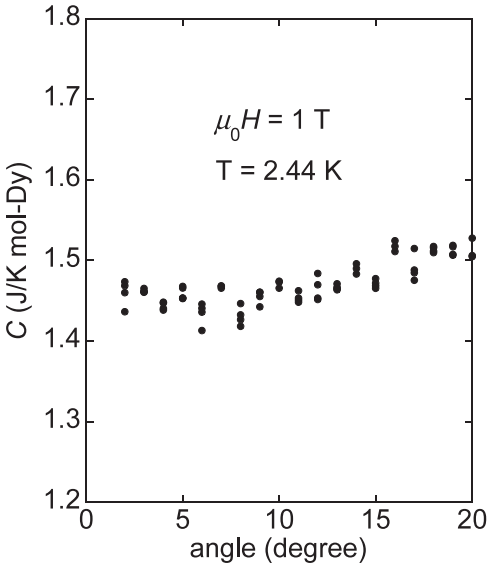

Figure 2. The angular dependence of the specific heat C of $Dy_2Ti_2O_7$ at 2.44 K. The minimum at about 6° corresponds to the accurate [111] alignment.

lattice [13, 14]. However, in the present case the residual entropy of this Kagome lattice is smaller than that of a pyrochlore lattice because spins on this Kagome lattice have the Kagome ice rule constraint that the 'up triangle' satisfies 2-in 1-out and the 'down triangle' satisfies 1-in 2-out (figure 1). Thus, this state may be called 'Kagome ice' [15]. Its residual entropy is estimated as $\frac{3}{4}k_B \ln[3^{N_A/3}(\frac{4}{9})^{N_A/3}] = \frac{1}{4}R \ln \frac{4}{3} \fallingdotseq 0.598\,\mathrm{J\,K^{-1}/(mol\ Dy)}$ by Pauling's method [8, 18]. R is the molar gas constant and N_A is the Avogadro number. Udagawa *et al* [16] calculated the exact value for the Kagome ice model with nearest-neighbour exchange to be $0.672\,\mathrm{J\,K^{-1}/(mol\ Dy)}$. Our previous experimental result, $0.44 \pm 0.12\,\mathrm{J\,K^{-1}/(mol\ Dy)}$ [8], was somewhat different from the calculation value.

We used a single-axis rotator in order to obtain the precise alignment along the [111] direction needed to stabilize the Kagome ice state. In the specific heat of the Kagome ice state, there are two peaks, one originating from the spin parallel to the field and the other from three frustrating spins. These two peaks are well separated at 1 T [17, 18]. Because the field is parallel to the direction of one of the four Ising spins for the exact [111] alignment, this spin has the maximum Zeeman energy. Thus the peak temperature becomes highest for the exact [111] field direction. Therefore, at a temperature below this peak temperature the specific heat attains a minimum for the exact alignment. A previous report [18] places this peak at around 6 K at 1 T. In figure 2 we show the angular dependence of the specific heat C at 2.44 K and at 1 T. At this temperature and field, the specific heat is expected to exhibit a minimum for the exact [111] alignment. In this way, we determined the exact alignment.

In figure 3, we show the temperature dependence of C/T at 0.5, 0.9 and 1 T along with the data at 1 T from our previous results [8]. The peak at 1 T is markedly sharper than those at 0.5 and 0.9 T. This sharp peak at 1 T should arise from the additional release of the difference in entropy between the Kagome ice state at low fields to the 1-in 3-out ordered state that has no residual entropy at high fields. The peak temperature, 400 mK, originating from frustrating spins on Kagome lattice is lower and the peak height is higher than those of the previous reports (figure 3 [8, 18]). This supports the assertion that the alignment in the present experiment is more accurate than those of the previous ones.

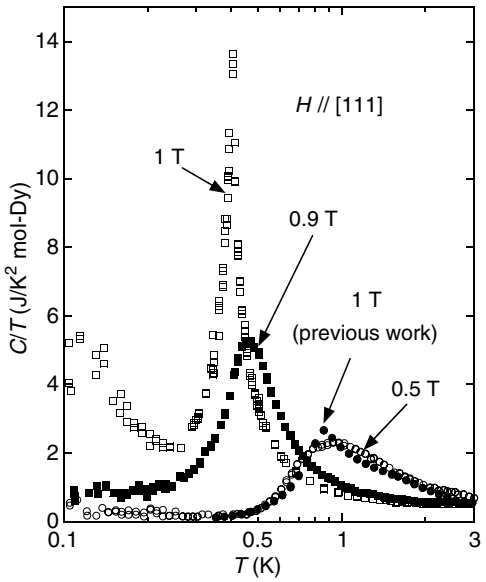

Figure 3. The temperature dependence of the specific heat divided by the temperature: C/T for $Dy_2Ti_2O_7$ at 0.5, 0.9, 1 T from this work and at 1 T from our previous report [8]. The field alignment is more accurate in the present study.

At 1 T, we additionally observed an anomalous upturn below 300 mK as shown in figure 3. This anomaly does not exist at 0.5 T and gradually develops above 0.9 T. This suggests that this upturn is related to the transition from the Kagome ice state to the 1-in 3-out ordered state. However, in the previous results at 1 T, C/T is about 0.1 J K^{-1}/(mol Dy) at 350 mK. This implies that accurate alignment is important to induce the additional increase at low temperatures.

In figure 4, we show the temperature dependence of the entropy. We estimated the entropy below 100 mK as the area of the triangle ($S(0.1\ \mathrm{K}) \approx \frac{1}{2}\frac{C_{\mathrm{spin}}(0.1\ \mathrm{K})}{T} \times 0.1\ \mathrm{K}$) and estimate $S(T)$ by integrating C/T from 0.1 to 3 K:

$$S(T) = S(0.1\ \mathrm{K}) + \int_{0.1\ \mathrm{K}}^{T} \frac{C_{\mathrm{spin}}}{T}\,\mathrm{d}T. \tag{1}$$

Since C above 3 K is not available, it is difficult to evaluate the exact total entropy of the Kagome ice state. However, in figure 4, at 3 K there is a difference between the entropy at 1 T and those at 0.5 and 0.9 T. In fact, $\Delta S(3\ \mathrm{K}) = S(1\ \mathrm{T}, 3\ \mathrm{K}) - S(0.9\ \mathrm{T}, 3\ \mathrm{K})$ reaches $\sim$0.5 J mol^{-1} K^{-2}. This is 80–90% of the expected value of the residual entropy of the Kagome ice state. Moreover, a noticeable entropy release occurs below 300 mK. There is a possibility that the residual entropy of the Kagome ice state is already partially released below 300 mK. However, in the previous report, down to 350 mK [8, 18], we and the earlier researchers observed residual entropy of the Kagome ice state. It is a task for the future to investigate the origin of the upturn (figure 3) which contributes to the large entropy release below 300 mK.

In conclusion, we measured the specific heat of the Kagome ice state down to 100 mK with more accurate alignment than in previous studies. We confirm that the sharp peak at 1 T originating from the three frustrating spins indicates entropy release of the entropy difference between the Kagome ice state at lower fields and the 1-in 3-out ordered state without residual entropy at higher fields. Moreover, we observed an anomalous upturn below 300 mK.

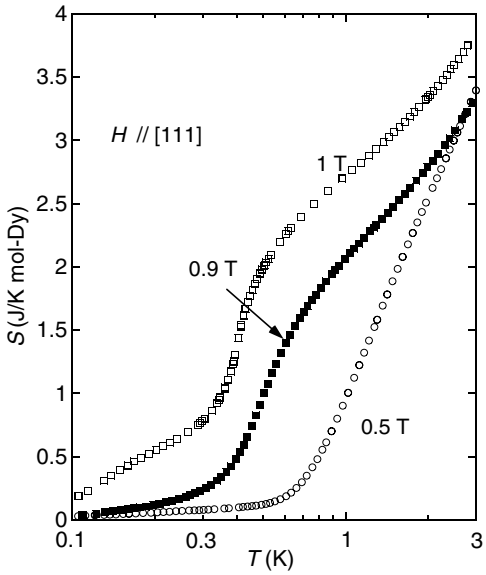

Figure 4. The temperature dependence of the entropy of $Dy_2Ti_2O_7$ up to 3 K.

Acknowledgments

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