Specific heat of single crystal of spin ice compound $Dy_2Ti_2O_7$

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Abstract

$Dy_2Ti_2O_7$ is regarded as a good example of geometrically frustrated spin systems exhibiting spin ice behavior. We report specific heat C_p of single crystalline $Dy_2Ti_2O_7$ in the characteristic magnetic-field direciton [100] down to 0.35 K and up to 5T. We observed a single peak in C_p with the peak temperature dependent on the field strength. For this direction, the component of the magentic moment parallel to the field is equivalent for every spin in each tetrahedron. Thus in high fields, this peak is expressed as a Schottky peak characterized by the Zeemann splitting; in lower fields, however, the peak becomes representative of the energy of spin-spin interactions.

Key words: $Dy_2Ti_2O_7$; Spin Ice; Specific heat; Pyrochlore

Recently, pyrochlore oxides $A_2B_2O_7$ have been recognized as important systems to study geometrical frustration. In $Dy_2Ti_2O_7$ the "spin ice" behavior has clearly been obeserved in the specific heat [1]. This material is thought to have macroscopically degenerate ground state because of the residual entropy and absence of long-range magnetic ordering down to 50 mK [1,2].

The macroscopically degenerate ground state of these materials can be represented by analogy with water ice. [3] In $Dy_2Ti_2O_7$, the A site ions, Dy^{3+}, constitute a corner-shared tetrahedral network. Because of the crystal-field effect, magnetic moments of the A site ions exhibit Ising anistropy along the local [111] direction. Furthermore, the effective nearest-neighbor ferromagnetic (FM) interaction makes the spin configuration of each tetrahedron to be 2-spins-in and 2-spins-out in the ground state. This constraint is referred to as the ice rule, and leads the ground state of this compound to be macroscopically degenerate with Pauling's entropy $(1/2)Rln(3/2)$ as the residual entropy [4].

Ramirez *et al*. [1] used polycrystalline sample of $Dy_2Ti_2O_7$ in their study of specific heat down to 0.25 K. There are three peaks in $C_{spin}(T)/T$ under magnetic field above 1.5 T. The peak temperatures are 0.34 K, 0.47 K and 1.12 K and independent of the field strength. In zero field, they found the residual entropy consistent with the expectation for the spin ice. They also found that the residual entropy readily disappears in magnetic field [1]. Because of the Ising anisotropy of Dy ions, the spin responses are different in the magnetic field along different directions. Therefore, it is important to investigate the physical properties of $Dy_2Ti_2O_7$ by using single crystals, in order to understand the origins of the specific heat peaks.

In this paper, we report the specific heat of single crystalline $Dy_2Ti_2O_7$ in the magnetic field. We focus on the data in the [100] field direction and examine the origin of the peak in the specific heat.

We grew single crystals of $Dy_2Ti_2O_7$ and $Eu_2Ti_2O_7$ by the floating zone method with an infrared furnace equipped with two ellipitical mirrors. The details of the crystal growth were reported previously [2]. We measured specfic heat between 0.35 and 40 K in fields up to 5 T by a relaxation method using a commercial calorimeter (Quantum Design, model PPMS).

The sample size was approximately $2.0 \times 2.0 \times 0.1 mm^3$ and the mass was about 1.5 mg. In order to avoid

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field inhomogenity due to demagnetization effect, we prepared a thin slice of a crystal with the (110) plane as the flat plane.

For $Dy_2Ti_2O_7$ the specific heat is expressed as,

$$C_{\rm total} = C_{\rm phonon} + C_{\rm spin} \quad (1)$$

$C_{\rm total}$, $C_{\rm phonon}$ and $C_{\rm spin}$ represent the total specific heat, the phonon contribution and the spin contribution, respectively. In order to estimate the phonon contribution, we measure specific heat of $Eu_2Ti_2O_7$ because this material is also insulating, nonmagnetic, and with the lattice parameter almost the same as that of $Dy_2Ti_2O_7$.

The energy gap for each Dy^{3+} ion between the nearly two-fold degenerate ground-state and the first exited state under crystal field is estimated to be approximately 150 K [5]. This permits us to consider only the nearly two-fold degenerate ground-state below 40 K. The energy scale of the nearest-neighbor FM interaction is estimated to be $J\_{\rm eff} = 1.2$ K in $Dy_2Ti_2O_7$ [6]. Along the [100] field direction, the components parallel to the field of four spins in each tetrahedron are equivalent. The value of $\cos\theta$ between the spin direction and the field direction is $1/\sqrt{3}$. Along this field direction the Zeemann energy at 1 T is expressed as $(1/\sqrt{3})g_{\rm J}J\mu_{\rm B}\mu_0 H_{\rm ext} = 3.8$ K. Thus, in fields higher than about 0.3 T the Zeemann energy becomes larger than the energy scale of the nearest-neighbor FM interaction. Therfore, we expect a Schottky-like specific heat with the characteristic energy changing from the internal FM interaction to the Zeemann energy given by the external field. In addition, we expect that there are no field independent peaks.

In Fig. 1 we show the specific heat of single-crystalline $Dy_2Ti_2O_7$ in the [100] field direction. The data at 0 T completely coincide with our polycrystalline data at 0 T(not shown) within experimental resolution. Spin freezing below 0.45 K is consistent with the result of the AC susceptibility $\chi_{\rm ac}$ [2]. There is a single peak with the peak temperature dependent on the field strength. This field dependent peak is attributable to the Schottky peak discussed above. Three peaks, which are independent of magnetic field and are observed in polycrystals, are not observed at all. This is consistent with our expectation, as we describe below.

Along the [100] field direction, we fit the data at 1, 2 and 5 T to the following Schottky formula,

$$\frac{C_{\rm spin}}{T} = \frac{N_{\rm A}k_{\rm B}}{T}\left(\frac{2\Delta E_0}{T}\right)^2 \frac{e^{2\Delta E_0/T}}{(1+e^{2\Delta E_0/T})^2} \quad (2)$$

We obtain $\Delta E_0 = 5(1)$, 9(1) and 20(1) K, respectively. The expected value of ΔE_0 is $1/\sqrt{3}g_{\rm J}J\mu_{\rm B}\mu_0 H_{\rm ext} = 3.88$, 7.76 and 19.4 K, respectivly. The experimental value above 2 T are in good agreement with the corresponding expected values. However, in lower fields, deviation from the behavior given by eq.(2) becomes evident. Correspondingly, the peak temperature becomes dominated by the energy of the nearest-neighbor FM interactions in lower fields.

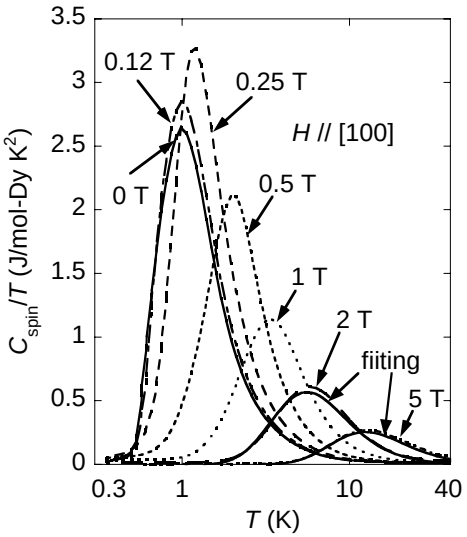

Fig. 1. Temperature dependence of the spin component of C/T in the [100] field direction down to 0.35 mK up to 5 T and Schottky fitting at 2 and 5 T.

In conclusion, we reported the specific heat of single crystalline $Dy_2Ti_2O_7$ down to 0.35 K under magnetic fields along the [100] direction. We observed only one peak in the specific heat in this field direction. With increasing field, we observed a changeover from the Schottky-like peak originating from effective FM nearest-neighbor interaction, $J_{\rm eff} = 1.2$ K, to that originating from the Zeemann energy associated with Ising spins Dy^{3+} determined by the external field.

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