Slow dynamics of Dy pyrochlore oxides Dy$_2$Sn$_2$O$_7$ and Dy$_2$Ir$_2$O$_7$

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Abstract. We report the magnetic properties of Dy pyrochlore oxides, Dy$_2$Sn$_2$O$_7$ and Dy$_2$Ir$_2$O$_7$. We show that the temperature dependence of the relaxation time $\tau(T)$ in the case of Dy$_2$Sn$_2$O$_7$ is very similar to that in the case of a typical spin ice, Dy$_2$Ti$_2$O$_7$. However, the time scale of Dy$_2$Sn$_2$O$_7$ is 10-100 times slower than that of Dy$_2$Ti$_2$O$_7$ over the entire temperature range. Dy$_2$Ir$_2$O$_7$ exhibits a metal-insulator transition at 134 K; it has a broad peak at 4.5 K in the DC magnetic susceptibility, indicating an antiferromagnetic correlation. However, the specific heat has no sharp anomaly at 4.5 K. We show that the Dy moments in Dy$_2$Ir$_2$O$_7$ have no long-range ordering down to 100 mK. We elucidate the anomalous slow dynamics that $\tau(T)$ decreases and becomes inhomogeneous below 12 K.

1. Introduction

Pyrochlore magnets with a local $(111)$ Ising magnetic anisotropy have been actively investigated owing to their strong geometrical frustration [1, 2, 3]. The ground state (GS) of Ising pyrochlore magnets is verified on the basis of theoretical studies [4]. The ferromagnetic coupling between the spins leads to stable spin configurations, with two spins in the outward direction and two spins in the inward direction (the 2-in 2-out state) in a basic tetrahedron. There are six possible combinations in this spin configuration for every tetrahedron; hence, the GS of the entire spin system is highly degenerate. A static disordered (spin ice) state is attained at low temperatures, in spite of the structural order of the lattice [5, 6]. On the other hand, the antiferromagnetic (AFM) coupling leads to the GS of long-range ordering (LRO), consisting of alternate tetrahedra with 4 inward spins or 4 outward spins (the 4-in 4-out state). However, the effects of electrical conductivity, spin-lattice coupling, c-f hybridization, etc. on the GS have not been verified. Further investigation of Ising pyrochlore magnets with a novel GS is required.

In this paper, we report the magnetic properties of Dy pyrochlore oxides, Dy$_2$Sn$_2$O$_7$ and Dy$_2$Ir$_2$O$_7$. In both compounds, the Dy$^{3+}$ ion has a large magnetic moment of $\sim 10\mu_B$ with a local $(111)$ Ising magnetic anisotropy. First, the insulating Dy$_2$Sn$_2$O$_7$ (Curie-Weiss temperature, $\Theta_{CW} = 1.69$ K) is considered as a spin ice compound because the anomaly in the AC magnetic properties is very similar to that of the typical spin ice compound, Dy$_2$Ti$_2$O$_7$, investigated in the previous study [7, 8]; the Sn$^{4+}$ ion is non-magnetic. However, there have been no reports on
the dynamics below 2 K thus far. In this study, we elucidate the slow spin dynamics below 2 K. Next, the semiconducting Dy$_2$Ir$_2$O$_7$ shows a metal-insulator transition (MIT) at $T_{MI} = 134$ K; we have adopted MIT for the sake of convenience. Recent studies have revealed that Ln$_2$Ir$_2$O$_7$ exhibits MITs, except for Ln = Pr [9]. In Ln$_2$Ir$_2$O$_7$, its electrical conductivity comes form the 5$d$ electrons from Ir$^{4+}$ as 4$f$ electrons are generally well localized. The MITs in Ln$_2$Ir$_2$O$_7$ involve a magnetic ordering of 5$d$ electrons; however, the origin of the MITs has not been verified thus far. Consequently, the magnetic degrees of freedom of the Dy moments of Dy$_2$Ir$_2$O$_7$ persist below $T_{MI}$. We show that Dy$_2$Ir$_2$O$_7$ with an AFM spin correlation has no LRO down to 100 mK and that it exhibits a novel slow dynamics below 12 K which are quite different from those of a spin ice.

2. Experimental Procedure

Single-phase polycrystalline samples of Dy$_2$Sn$_2$O$_7$ and Dy$_2$Ir$_2$O$_7$ were prepared by a standard solid-state reaction method. For Dy$_2$Sn$_2$O$_7$, the sample was prepared in the same manner as the previous report [7]. For Dy$_2$Ir$_2$O$_7$, the mixture was prepared using Dy$_2$O$_3$(99.99%) and IrO$_2$ (Tanaka Kikinzoku Kogyo). The molar ratio of Dy to Ir was 1:1:1. The mixture was pressed into pellets, which were then inserted into a Pt tube and heated at 1423-1523 K for around 10 days in a vacuum silica tube with several intermediate grindings. After adding 10 mol% of IrO$_2$, the process was continued for four days with several intermediate grindings. Then, the last step described above was repeated.

The reaction products were identified by powder X-ray diffraction (XRD) measurements. The XRD pattern indicated a single phase with a cubic pyrochlore structure. DC magnetizations down to 2 K were measured using a commercial SQUID magnetometer (MPMS, Quantum Design (QD) Inc.). The AC magnetic susceptibilities, $\chi_{AC}$, were measured using the ACMS option in PPMS (QD Inc.) at 1.8-300 K. $\chi_{AC}$ below 1.8 K was measured using a SQUID magnetometer developed at the Institute Néel, CNRS, Grenoble. Specific heat measurements down to 0.35 K were performed by the thermal relaxation method (PPMS, QD Inc.).

3. Results and Discussion

3.1. Slow dynamics of spin ice type in Dy$_2$Sn$_2$O$_7$

Figures 1(a) and (b) show the temperature dependence of $\chi_{AC}$ for Dy$_2$Sn$_2$O$_7$ in an AC field of 1.4 Oe. The real part, $\chi'$, and the imaginary part, $\chi''$, are highly dependent on the frequency. $\chi'$ at 0.005 Hz shows a broad maximum at 0.75 K, and $\chi''$ shows a peak below 0.65 K. As the frequency increases, the maximum of $\chi'$ and the peak of $\chi''$ shift toward higher temperatures. The temperature dependence of the DC magnetic susceptibility, $M/H$, of Dy$_2$Sn$_2$O$_7$ at 100 Oe, measured under the zero-field-cooled (ZFC) and field-cooled (FC) conditions, is also shown in Fig. 1(a). The irreversibility is clearly visible below $T_I \sim 0.65$ K. The ZFC curve has a sharp peak at $T_I$, and it steeply falls toward zero. On the other hand, the FC curve rises monotonically on cooling below $T_I$. This result is in agreement with the reported behavior of spin ice compounds [10, 11]. Thus, on cooling, Dy$_2$Sn$_2$O$_7$ exhibits slow spin dynamics without any LRO down to 100 mK.

It is important to study the slow dynamics in order to determine the temperature dependence of the relaxation time $\tau(T)$. We can estimate $\tau(T)$ from the frequency dependence of $\chi''(f)$. In the case of Debye relaxation with a single dispersion, $\chi''(f)$ becomes a symmetric function of log $f$, and it is maximum at the frequency defined by $1/2\pi\tau$, where $\tau$ is a characteristic relaxation time. The frequency dependence of $\chi''$ at various $T$ is shown in Figs. 2(a) and 2(b). The experimental result is a slight asymmetric function of log $f$; hence, a narrow distribution is expected down to the lowest temperature. Therefore, the approximate $\tau(T)$ is obtained from the maximum frequency $f_m$ in $\chi''(f)$, $\tau = 1/2\pi f_m$. Furthermore, from the frequency dependence of the peak temperature $T_p$ of $\chi''(T)$ in Fig. 1(b), we can determine $\tau$ at $T_p$ by using $\tau = 1/2\pi f$. 


Figure 1. (a) Temperature dependence of $M/H$ and $\chi'$ of Dy$_2$Sn$_2$O$_7$. ZFC and FC denote zero-field cooling and field cooling, respectively. (b) Temperature dependence of $\chi''$ of Dy$_2$Sn$_2$O$_7$.

Figure 2. Frequency dependence of $\chi''(f)$ (a) below 1.2 K and (b) above 1.8 K.

Figure 3 shows $\tau(T)$ of Dy$_2$Sn$_2$O$_7$. The data show three distinct features. At temperatures above 10 K, $\tau(T)$ increases on cooling. In the temperature range of 2-10 K, $\tau(T)$ is virtually constant. Below 2 K, $\tau(T)$ increases again. For comparison, $\tau(T)$ of spin ice compounds are shown in Fig. 3 [10, 11, 12]. It should be noted that our definition of $\tau$ estimated by $\chi_{AC}$ is different from the definition ($\tau = 1/f_m$) provided by Snyder et al. [12]; in general, our definition is used. The characteristics of $\tau(T)$ in the case of Dy$_2$Sn$_2$O$_7$ are very similar to those in the case of Dy$_2$Ti$_2$O$_7$. The present result strongly indicates that Dy$_2$Sn$_2$O$_7$ is a spin ice compound.

Next, we discuss the dynamics. Above 20 K, $\tau(T)$ is effectively explained on the basis of the Arrhenius law, with the energy barrier $E_B = 246$ K. We can consider that $E_B$ corresponds to the energy of the excited levels in the crystalline electric field (CEF); this is related to Ising anisotropy [13]. The plateau regions of $\tau(T)$ in the temperature range of 2-10 K is explained by the quantum tunneling process through non-zero off-diagonal components of the dipolar interaction from neighboring moments [13]. The tunneling rate for Dy$_2$Sn$_2$O$_7$ is approximately $10^{-2}$ s. This is speculatively attributed to a difference between the dipolar interaction and the CEF level scheme. Below 2 K, the spin ice state is attained by the development of a short-ranged spin correlation. It should be noted that the time scale of Dy$_2$Sn$_2$O$_7$ is 10-100 times slower than that of Dy$_2$Ti$_2$O$_7$ over the entire temperature range. The dynamics of Dy$_2$Sn$_2$O$_7$ are much
slower than those of Dy$_2$Ti$_2$O$_7$.

Figure 3. $\tau(T)$ of Dy$_2$Sn$_2$O$_7$. The data for Ho$_2$Ti$_2$O$_7$ and Ho$_2$Sn$_2$O$_7$ in the previous report are shown [10]. For Dy$_2$Ti$_2$O$_7$, the data above 1.8 K in the previous report are shown [11]. Data below 2 K for both powder and single crystal samples are shown [14].

3.2. Novel slow dynamics of Dy$_2$Ir$_2$O$_7$

The temperature dependence of the magnetization $M(T)$ for Dy$_2$Ir$_2$O$_7$, measured under ZFC and FC conditions, is shown in Fig. 4(a). A slight difference between the FC and ZFC curves appears below $T_{MI} = 134$ K. This anomaly is caused by the appearance of a very weak ferromagnetic component ($\sim 10^{-3} \mu_B$/f.u.) due to an unsolved magnetic ordering of Ir moments in MIT. The inset shows the reciprocal magnetic susceptibility $(M/H)^{-1}$ under the ZFC condition below 60 K. $(M/H)^{-1}$ exhibits Curie-Weiss behavior; hence, assuming the Curie-Weiss law at 20-60 K, the effective moment and $\Theta_{CW}$ are estimated to be $10.27 \mu_B$ and $-3.4$ K, respectively. The effective moment is virtually in perfect agreement with the value of Dy$_2$Sn$_2$O$_7$; hence, the major contribution of DC magnetization below $T_{MI}$ is attributed to the Dy moments. Furthermore, the degrees of freedom of the Dy moments persist much below $T_{MI}$. Then, the negative value of $\Theta_{CW}$ indicates an AFM coupling between the Dy moments. On cooling, $M(T)$ has a broad maximum at 4.5 K. In addition, a large difference between the FC and ZFC curves appears below 0.8 K. Under the ZFC condition, $M(T)$ has a broad peak at 0.77 K, and it decreases toward a finite value. On the other hand, under the FC condition, $M(T)$ is virtually constant below 0.8 K. The results suggest a partial freezing of the Dy moments.

Figure 4(b) shows the magnetic contribution of the specific heat $C_m/T$ and the magnetic entropy $S_m$ for Dy$_2$Ir$_2$O$_7$. In order to obtain the magnetic contribution $C_m$, we subtracted the lattice contribution by using the lattice specific heat of Eu$_2$Ir$_2$O$_7$. $C_m/T$ shows a broad peak at 2.5 K. However, no sharp anomaly is observed at 4.5 K, where $M(T)$ shows a maximum. As $S_m$ reaches $\sim 5.5$ J/K Dy-mole ($\sim 0.95$Rln2) at 20 K, the entropy due to the CEF GS doublet of Dy$^{3+}$ is released below 20 K; there is no residual entropy, as in the case of a spin ice.

From the results presented above, we can conclude that the dynamics of Dy$_2$Ir$_2$O$_7$ are different from those of a spin ice. Figure 5(a) shows the temperature dependence of $\chi_{AC}$ of Dy$_2$Sn$_2$O$_7$ in an AC field of 5 Oe. The anomaly around 20 K is very similar to that of Dy$_2$Sn$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$. As the frequency is lower, the maximum of $\chi'(T)$ and the peak of $\chi''(T)$ ($T_{HT_{\text{max}}}$) shift toward lower temperatures. On the other hand, $\chi'(T)$ at 10 Hz shows a broad maximum at 4.5 K; this is consistent with the anomaly in DC magnetization. However, as the frequency is higher, the maximum at 4.5 K at 10 Hz and the broad peak of $\chi''(T)$ ($T_{LT_{\text{max}}}$) shift to lower temperatures. Thus, the dynamics involved in this anomaly become fast on cooling. This feature is not responsible for a simple thermal process. The frequency dependence of $\chi''$ at various $T$ is shown in Fig. 5(b). On cooling, the maximum frequency shifts to lower frequencies down to
12 K; below 12 K, it shifts to higher frequencies. To investigate the slow dynamics of Dy$_2$Ir$_2$O$_7$, we estimated $\tau(T)$ of Dy$_2$Ir$_2$O$_7$ from the data of $\chi_{AC}$, as in the case of Dy$_2$Sn$_2$O$_7$.

Figure 4. (a) $M(T)$ for Dy$_2$Ir$_2$O$_7$ measured under ZFC and FC conditions. The inset shows $(M/H)^{-1}$ under the ZFC condition below 60 K. (b) $C_m/T$ and $S_m$ for Dy$_2$Ir$_2$O$_7$.

Figure 5. (a) Temperature dependence of $\chi_{AC}$ for Dy$_2$Ir$_2$O$_7$ at 10k, 3k, 1k, 500, 190, 80, 35, and 10 Hz. (b) Frequency dependence of $\chi''$ for Dy$_2$Ir$_2$O$_7$ at various $T$.

Figure 6 shows $\tau(T)$ of Dy$_2$Ir$_2$O$_7$. Above 20 K, $\tau(T)$ is effectively explained on the basis of the Arrhenius law, with $E_B = 260$ K. This value is virtually the same as that of Dy$_2$Sn$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$. Therefore, we can assume that the anomaly is responsible for the Ising anisotropy of Dy moments. Above 16 K, $\tau(T)$ estimated by a maximum of $\chi''(f)$ corresponds to $\tau$ estimated by the peak of $\chi''(T)$. However, a discrepancy between their estimated $\tau$ appears below 16 K. On cooling, $\tau(T)$ shows a maximum at around 12 K, and it becomes short. This implies that $\tau$ is widely distributed below 12 K; the system becomes inhomogeneous below 12 K. Dy moments with a long component in $\tau$ cause the freezing in $M(T)$, as shown in Fig. 4(a). The other Dy moments with a short component in $\tau$ keep fluctuating slowly down to 100 mK. To the best of our knowledge, the appearance of fast dynamics below 12 K in this study is a novel observation in the field of magnetism.

Next, we discuss the origin of the anomalous dynamics. Although the local spin correlation between the Dy moments is AFM, there is no LRO down to 100 mK. Hence, we may speculate
that a short-ranged ordering of the 4-in 4-out state is realized in the GS. At a finite temperature, the 1-in 3-out (or 3-in 1-out) and 2-in 2-out states are favored because they are highly degenerated states. From a point of view of the magnetic monopole picture, many pairs of magnetic monopoles are created on cooling, as opposed to the case of a spin ice [15]. It is speculated that this change in the spin configuration at a finite temperature is related to the anomalous dynamics. Furthermore, a slight structural change caused by MIT and an effect of an internal field induced by a magnetic ordering of 5d electrons below $T_{MI}$, should also be considered. Further investigation is required to verify the origin.

![Temperature dependence of relaxation time $\tau(T)$ for Dy$_2$Ir$_2$O$_7$. $\tau(T)$ of Dy$_2$Ti$_2$O$_7$ and Dy$_2$Sn$_2$O$_7$ are shown for comparison. The data points are the same as those in Fig. 3.](Figure 6)

Figure 6. Temperature dependence of relaxation time $\tau(T)$ for Dy$_2$Ir$_2$O$_7$. $\tau(T)$ of Dy$_2$Ti$_2$O$_7$ and Dy$_2$Sn$_2$O$_7$ are shown for comparison. The data points are the same as those in Fig. 3.

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