RAPID COMMUNICATION

High pressure synthesis and characterization of the pyrochlore $Dy_2Pt_2O_7$: A new spin ice material*

Qi Cui(崔琦)[1,2], Yun-Qi Cai(蔡云麒)[1,2], Xiang Li(李翔)[3,4], Zhi-Ling Dun(顿志凌)[5,6], Pei-Jie Sun(孙培杰)[1,2,7], Jian-Shi Zhou(周建十)[3], Hai-Dong Zhou(周海东)[5], and Jin-Guang Cheng(程金光)[1,2,7,†]

[1] *Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*
[2] *School of Physical Sciences, University of Chinese Academy of Sciences, Beijing* 100190, *China*
[3] *Materials Science and Engineering Program, Mechanical Engineering, University of Texas at Austin, Austin, Texas* 78712, *USA*
[4] *Key Laboratory of Advanced Optoelectronic Quantum Architecture and Measurement of Ministry of Education, School of Physics, Beijing Institute of Technology, Beijing* 100081, *China*
[5] *Department of Physics and Astronomy, University of Tennessee, Knoxville, TN* 37996, *USA*
[6] *School of Physics, Georgia Institute of Technology, Atlanta, GA* 30332, *USA*
[7] *Songshan Lake Materials Laboratory, Dongguan* 523808, *China*

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The cubic pyrochlore $Dy_2Pt_2O_7$ was synthesized under 4 GPa and 1000 °C and its magnetic and thermodynamic properties were characterized by DC and AC magnetic susceptibility and specific heat down to 0.1 K. We found that $Dy_2Pt_2O_7$ does not form long-range magnetic order, but displays characteristics of canonical spin ice such as $Dy_2Ti_2O_7$, including (1) a large effective moment 9.64 μ_B close to the theoretical value and a small positive Curie–Weiss temperature $\theta_{CW} = +0.77$ K signaling a dominant ferromagnetic interaction among the Ising spins; (2) a saturation moment ~4.5 μ_B being half of the total moment due to the local ⟨111⟩ Ising anisotropy; (3) thermally activated spin relaxation behaviors in the low (~1 K) and high (~20 K) temperature regions with different energy barriers and characteristic relaxation time; and most importantly, (4) the presence of a residual entropy close to Pauling's estimation for water ice.

Keywords: $Dy_2Pt_2O_7$, pyrochlore oxide, spin ice, high-pressure synthesis

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1. Introduction

Geometrically frustrated magnets can display rich and diverse phenomena, providing an excellent platform for experimental realizations of collective magnetism that was predicated theoretically.[1,2] The recognition of a spin ice state in the cubic pyrochlore compounds $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ represents such an example that successfully maps to the well-known water–ice problem.[3–6] In these pyrochlores, the magnetic rare-earth ions, Ho^{3+} or Dy^{3+}, with a large magnetic moment of $\sim 10\mu_B$ reside on the vertices of the corner-sharing tetrahedra, forming a geometrically frustrated lattice. A uniaxial local crystalline electric field (CEF) around Ho^{3+} or Dy^{3+} results in a nearly perfect easy-axis anisotropy, forcing the rare-earth's spin to point along the local ⟨111⟩ axis that joins the centers of two neighboring tetrahedra.[7,8] The combination of dipolar and magnetic exchange interactions favors 'two-in, two-out' spin configurations on each tetrahedron, which has been termed 'spin ice' in direct analogy to the 'two-short, two-long' proton bond disorder in water ice. The Pauling's zero-point entropy $S_P = (R/2)\ln(3/2)$, where R is the ideal gas constant, for water ice has also been confirmed in the spin ices having a macroscopically degenerate ground state.[5]

The low-temperature magnetic properties of a pyrochlore spin ice are mainly controlled by the magnetic exchange (J_{nn}) and the dipole–dipole interaction (D_{nn}) of the nearest-neighbor spins. For these pyrochlore spin ice materials, J_{nn} is usually antiferromagnetic, while D_{nn} is ferromagnetic and can be calculated as $D_{nn} = 5/3(\mu_0/4\pi)\mu^2/r_{nn}^3$, where r_{nn} is the nearest-neighbor rare-earth distance. D_{nn} is estimated to be ~ 2.35 K for $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. The physics of pyrochlore spin ices can be largely captured by the dipolar spin ice model (DSIM) proposed by den Hertog and Gingras.[9] In the theoretical phase diagram based on DSIM,[9] the spin ice state is stable for $J_{nn}/D_{nn} > -0.91$, and a $Q = 0$ antiferromagnetically ordered state is favored for $J_{nn}/D_{nn} < -0.91$. Since J_{nn} is more sensitive to r_{nn} than D_{nn}, by synthesizing $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$,[10,11] which have smaller lattice parameter in comparison to the corresponding titanates and stannates, our previous studies have successfully modified the ratio of J_{nn}/D_{nn}. The lowest value of -0.73 is achieved in $Dy_2Ge_2O_7$,[11] which

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†Corresponding author. E-mail: jgcheng@iphy.ac.cn

is still located inside the spin ice regime. A further enhancement of J_{nn} is needed in order to achieve a transition from spin ice to a $Q = 0$ state.

Besides the chemical pressure effects caused by the size of B-cation in $Ln_2B_2O_7$ (Ln = rare earth), our recent studies on the platinum-based pyrochlores $Ln_2Pt_2O_7$ have revealed an additional effect of the nonmagnetic Pt^{4+} ions,[12,13] i.e., the spatially more extended Pt-5d orbitals and thus the enhanced Pt 5d–O 2p hybridizations can modify the CEF and influence the exchange interactions. In comparison with $Gd_2B_2O_7$ (B = Ge, Ti, Sn), the antiferromagnetic transition temperature of $Gd_2Pt_2O_7$ is substantially enhanced because the empty Pt-e_g orbitals provide extra superexchange pathways.[13] Thus, we expect an alternative routine to modify J_{nn}/D_{nn} in the Pt-based Ising pyrochlores.

In this work, we have prepared the pyrochlore compound $Dy_2Pt_2O_7$ under high pressure, and characterized its magnetic and thermodynamic properties via magnetic susceptibility and specific heat measurements down to 0.1 K. We find that $Dy_2Pt_2O_7$ does not exhibit any long-rang magnetic order at low temperature, but displays canonical spin ice characteristics, including the thermally activated spin dynamics and the presence of Pauling's zero-point entropy. By comparing the low-temperature magnetic specific heat to DSIM, we obtain a ratio of $J_{nn}/D_{nn} = -0.56$ for $Dy_2Pt_2O_7$. Our results demonstrate that $Dy_2Pt_2O_7$ is a new spin ice compound with enhanced superexchange interaction J_{nn}.

2. Experimental details

The sample preparations and characterizations in the present study are similar to those performed in our previous work.[12] The cubic pyrochlore $Dy_2Pt_2O_7$ sample was prepared under 4 GPa and 1000 ℃ by using a Kawai-type multi-anvil module (Max Voggenreiter GmbH). The resultant high-pressure products were first washed with warm aqua regia to remove a small amount of platinum metal and unreacted Dy_2O_3; the obtained powders were then pressed into pellets and subjected to heat treatment at 900 ℃ for 10 h to facilitate the measurements of the bulk physical properties.

Phase purity of the obtained powder and pellet samples was examined by powder x-ray diffraction (XRD) at room temperature. Structural parameters were extracted from the XRD patterns via Rietveld refinement with the FullProf program. DC magnetic susceptibility was measured with a commercial magnetic property measurements system (MPMS-III, Quantum Design) in the temperature range from 1.8 K to 300 K under an external magnetic field of $\mu_0 H = 0.1$ T. AC magnetic susceptibility measurements in the temperature range 2 K$< T <$ 50 K were performed in a physical property measurement system (PPMS, Quantum Design). AC susceptibility measurements from 70 mK to 2 K were carried out in an Oxford dilution refrigerator with the mutual induction method; an excitation current of $\sim$ 1 mA with frequencies ranging from 117 Hz to 1517 Hz was applied to the primary coil during the measurements. Specific-heat data down to 0.1 K were collected by the PPMS with a dilution refrigerator insert.

3. Results and discussion

3.1. Structure characterizations

Figure 1 (a) shows the powder XRD pattern of $Dy_2Pt_2O_7$, which is confirmed to be single phase with the pyrochlore structure. The XRD pattern can be refined well with a cubic pyrochlore structure defined by the Fd-3m (No. 227) space group with the Dy atom at 16d $(1/2, 1/2, 1/2)$, the Pt atom at 16c $(0, 0, 0)$, the O1 atom at 48f $(x, 1/8, 1/8)$, and the O2 atom at 8b $(3/8, 3/8, 3/8)$ site, respectively. The obtained lattice constant $a = 10.1913(1)$ Å for $Dy_2Pt_2O_7$ is in excellent agreement with the previously reported value of 10.202 Å.[14] In addition, the lattice constant a scales linearly with the ionic radius (IR) of the B^{4+} ions for the series of $Dy_2B_2O_7$ (B = Sn, Pt, Ti, Ge), as depicted in Fig. 1(b).

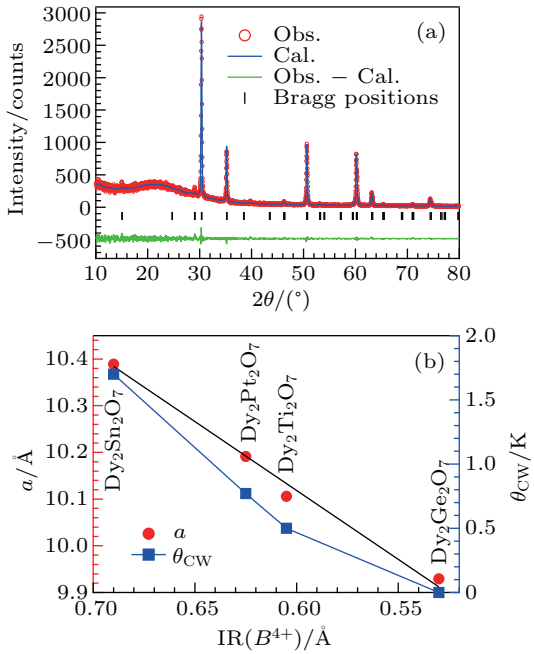

Fig. 1. (a) Room-temperature powder XRD pattern of $Dy_2Pt_2O_7$ and the results of the Rietveld refinement. (b) Lattice parameter a (left) and the Curie–Weiss temperature θ_{CW} (right) as a function of the ionic radius of the B^{4+} ions in the series of $Dy_2B_2O_7$ (B = Sn, Pt, Ti, Ge).

3.2. DC magnetic susceptibility

The magnetic properties of $Dy_2Pt_2O_7$ were first characterized by DC magnetization measurements in the temperature range from 1.8 K to 300 K. Figure 2(a) displays the DC magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ measured under $\mu_0 H = 0.1$ T after zero-field-cooled (ZFC) and field-cooled (FC) processes from room temperature. No sign of long-range magnetic ordering was observed down to 1.8 K.

A Curie–Weiss (CW) fitting has been applied to $\chi^{-1}(T)$ in the temperature range 10–50 K, i.e., $\chi^{-1}(T) = (T - \theta_{CW})/C$, which yields an effective moment $\mu_{eff} = 9.62\ \mu_B$ per Dy^{3+} and a CW temperature $\theta_{CW} = +0.77$ K for $Dy_2Pt_2O_7$. The obtained μ_{eff} is very close to the theoretical value of 9.55 μ_B for free Dy^{3+} ion with $J = 15/2$, and the small positive θ_{CW} signals a net ferromagnetic interaction between the Ising spins located on the vertices of the corner-shared tetrahedra.[15] As seen in Fig. 1(b), the positive θ_{CW} decreases roughly linearly with decreasing IR of B^{4+} and approaches to zero for the Ge-based pyrochlore. Such a monotonic variation of θ_{CW} versus IR(B^{4+}) suggests that the nearest-neighbor distance, r_{nn}, remains the dominant factor that governs the balance between the antiferromagnetic J_{nn} and the ferromagnetic D_{nn} between the nearest-neighbor Ising spins.

The isothermal magnetization $M(H)$ curves measured in fields up to 5 T at 2 K and 5 K are shown in Fig. 2(b) for $Dy_2Pt_2O_7$. As seen in the classical spin ices, a typical ferromagnetic behavior is observed and the saturation moment reaches $\sim 4.5\ \mu_B$ per Dy^{3+}, which is about half of the total moment available at each site due to the local $\langle 111 \rangle$ Ising magnetic anisotropy and the powder averaging.[16] From these DC magnetic measurements on $Dy_2Pt_2O_7$, we find nearly identical behaviors as those well-characterized classical spin ices $Dy_2B_2O_7$ (B = Sn, Ti, Ge). Below we further provide the AC magnetic susceptibility and thermodynamics evidences in support of the spin-ice behavior for $Dy_2Pt_2O_7$.

3.3. AC magnetic susceptibility

Figure 3 shows the AC magnetic susceptibility of $Dy_2Pt_2O_7$ in the temperature range (a)–(c) below 2 K and (d)–(f) above 2 K. For $T < 2$ K, the real $\chi'(T)$ and the imaginary part $\chi''(T)$ are normalized by their maximum values.

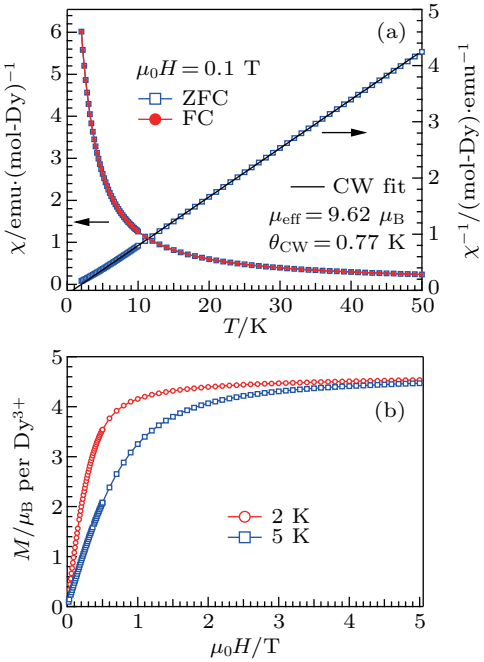

Fig. 2. (a) Temperature dependence of the DC magnetic susceptibility $\chi(T)$ and its inverse $\chi^{-1}(T)$ for $Dy_2Pt_2O_7$. The solid line represents the Curie–Weiss fitting curve and the fitting parameters are given in the figure. (b) The isothermal magnetization curves $M(H)$ measured at $T = 2$ K and 5 K for $Dy_2Pt_2O_7$.

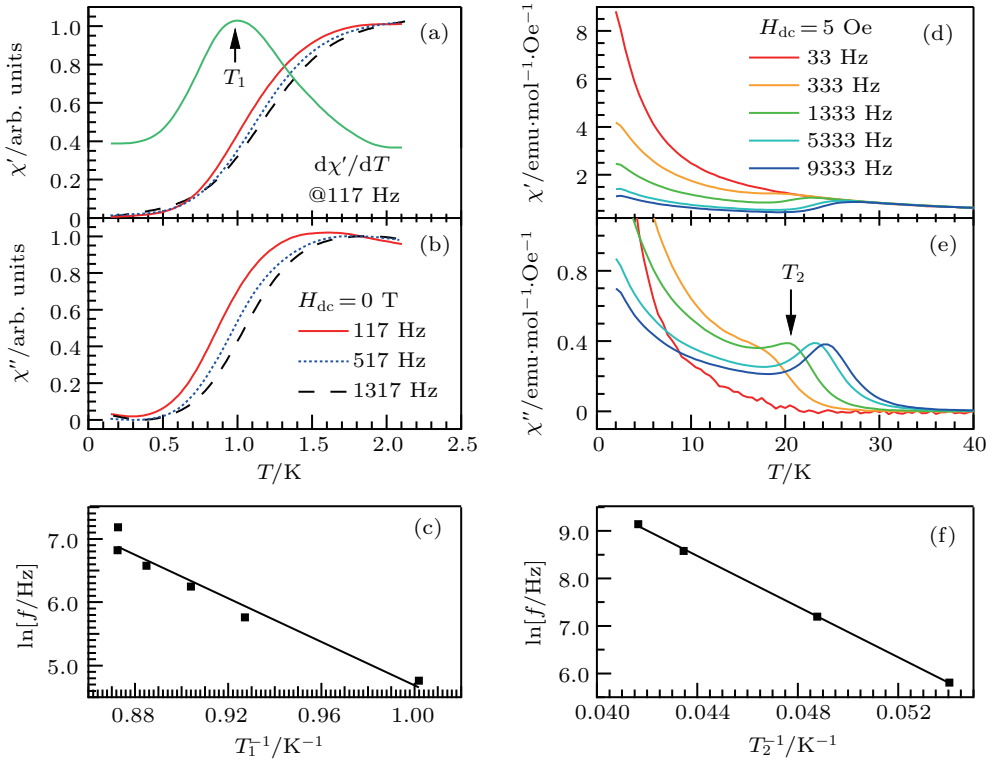

Fig. 3. The real part $\chi'(T)$ and the imaginary part $\chi''(T)$ of the AC magnetic susceptibility for $Dy_2Pt_2O_7$ in the temperature range (a), (b) below 2 K and (d), (e) above 2 K. (c) and (f) The linear fit to the Arrhenius plot of the characteristic temperatures T_1 and T_2, respectively.

As can be seen in Figs. 3(a) and 3(b), $\chi'(T)$ in the frequency range from 117 Hz to 1317 Hz drops quickly below ~ 1.6 K, and $\chi''(T)$ displays a broad shoulder at a slightly lower temperature. Both $\chi'(T)$ and $\chi''(T)$ are frequency dependent and the shoulder shifts to higher temperatures upon increasing frequency. Such a slow spin dynamics is typical for classical spin ices and has been attributed to the formation of spin-ice configurations.[17,18] Due to the ambiguity of the maximum in $\chi''(T)$, here we define the maximum of $\mathrm{d}\chi'/\mathrm{d}T$ as a characteristic temperature T_1 whose frequency dependence can be fitted with an Arrhenius formula, $f = f_{01}\exp(-E_{a1}/\kappa_B T_1)$, Fig. 3(c), yielding an activation energy $E_{a1}^{Dy} = 17.2(1.8)$ K and a characteristic relaxation time $\tau_{01}^{Dy} = 1/f_{01}^{Dy} = 3.18\times10^{-10}$ s.

Another distinct feature in the AC susceptibility of Dy-pyrochlore spin ices is the presence of a high-temperature peak around 15 K.[17–20] Similar behaviors are also observed in $Dy_2Pt_2O_7$, Figs. 3(d) and 3(e). For $f \geq 333$ Hz, we observe a clear drop in $\chi'(T)$ and a corresponding maximum in $\chi''(T)$ at temperature T_2, which starts at ~ 18 K and moves to higher temperatures with increasing frequency. Similarly, a linear fitting to the Arrhenius plot of $\ln f$ versus $1/T_2$, Fig. 3(f), gives the activation energy $E_{a2}^{Dy} = 267(4)$ K and the characteristic relaxation time $\tau_{02}^{Dy} = 1/f_{02}^{Dy} = 1.66\times10^{-9}$ s, which are also consistent with the reported values of $E_a = 210$ K and $\tau_0 = 1.39\times10^{-9}$ s for the polycrystalline $Dy_2Ti_2O_7$.[20] Since the energy barrier $E_{a2} \sim 300$ K is close to the energy scale set by the first excited CEF level from the ground state doublet, the spin relaxation processes are thermally activated for $T \geq T_2$.

3.4. Specific heat

Figure 4(a) shows the low-temperature specific heat $C(T)$ of $Dy_2Pt_2O_7$, which displays a Schottky-like peak centered at about 1.1 K. Both the peak position ~ 1 K and the magnitude ~ 3 J·(mol-Dy)$^{-1}$·K^{-1} are very similar to those of the classical Dy-pyrochlore spin ices, $Dy_2B_2O_7$ (B = Sn, Ti, Ge).[11] The magnetic contribution C_m was obtained by subtracting from the measured total specific heat C_{total} the lattice contribution C_{lat}, which was taken from the specific heat of isostructural, nonmagnetic $Lu_2Pt_2O_7$. As shown in Fig. 4(a), the magnetic entropy obtained via integrating C_m/T over the investigated temperature range approaches a constant value of ~ 4.2 J·(mol-Dy)$^{-1}$·K^{-1}, which falls considerably short of the expected value of $R\ln2 \approx 5.76$ J·(mol-Dy)$^{-1}$·K^{-1} for Dy^{3+} with a ground Karmers doublet. The resultant residual entropy 1.56 J·(mol-Dy)$^{-1}$·K^{-1} is close to the Pauling's zero-point entropy $S_P = (R/2)\ln(3/2) = 1.68$ J·(mol-Dy)$^{-1}$·K^{-1}, providing an important evidence for the spin-ice state in $Dy_2Pt_2O_7$.[5]

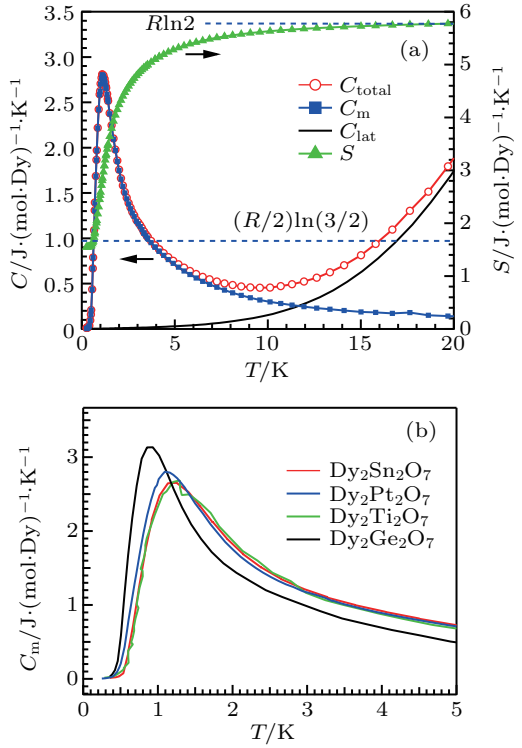

Fig. 4. (a) Specific heat $C(T)$ of $Dy_2Pt_2O_7$. The $C(T)$ of isostructural, nonmagnetic $Lu_2Pt_2O_7$ was used as the lattice contribution C_{lat}. The magnetic contribution C_m was obtained by subtracting C_{lat} from the measured total C_{total}. The entropy S was evaluated by integrating C_m/T over the investigated temperature range. (b) Comparison of the magnetic specific heat C_m of $Dy_2B_2O_7$ (B = Sn, Pt, Ti, Ge) pyrochlores.

3.5. Discussion

Based on these above characterizations, we can conclude that $Dy_2Pt_2O_7$ is a new spin ice characterized by: (i) a large effective moment 9.64 μ_B close to the theoretical value, and a small positive Curie–Weiss temperature $\theta_{CW} = +0.77$ K signaling a dominant ferromagnetic interaction among the Ising spins; (ii) a saturation moment ~ 4.5 μ_B being half of the total moment due to the local $\langle 111\rangle$ Ising anisotropy; (iii) thermally activated spin relaxation behaviors in the low (~ 1 K) and high (~ 20 K) temperature regions with different energy barriers and characteristic relaxation time; and most importantly, (iv) the presence of a residual entropy close to Pauling's estimation for water ice.

Although it is not unexpected that $Dy_2Pt_2O_7$ displays typical behaviors of canonical spin ice, the effects of nonmagnetic Pt^{4+} are noteworthy. For this purpose, we have compared the C_m of $Dy_2Pt_2O_7$ with those of $Dy_2B_2O_7$ (B = Sn, Ti, Ge) in Fig. 4(b). For those latter spin ices, it has been shown that the C_m peak shifts to lower temperatures and its height also increases upon reducing the ionic radius of B^{4+} ions or r_{nn}.[11] This is consistent with the prediction of DSIM due to the enhancement of J_{nn} with respect to D_{nn}.[9] If considering only the lattice parameter or r_{nn}, the C_m peak of $Dy_2Pt_2O_7$ should locate in between those of $Dy_2Sn_2O_7$ and $Dy_2Ti_2O_7$. However, as shown in Fig. 4(b), the C_m peak of $Dy_2Pt_2O_7$ is higher than that of $Dy_2Sn_2O_7$ and $Dy_2Ti_2O_7$, and the C_m

peak also occurs at a lower temperature than the other two. Based on the prediction of DSIM[9] and $D_{nn} \approx 2.29$ K for $Dy_2Pt_2O_7$, the C_m peak temperature $T_{peak} = 1.13$ K corresponds to a $J_{nn}/D_{nn} = -0.56$, which predicts $J_{nn} = -1.28$ K and $J_{eff} = J_{nn} + D_{nn} = 1.01$ K. These values are also listed in Table 1. For comparison, $Dy_2Ti_2O_7$ has $J_{nn}/D_{nn} = -0.49$, $J_{nn} = -1.15$ K, and $J_{eff} = 1.20$ K.[11] Because the ionic radius of Pt^{4+} (0.625 Å) is larger than that of Ti^{4+} (0.605 Å), the observed larger $|J_{nn}|$ and $|J_{nn}/D_{nn}|$ in $Dy_2Pt_2O_7$ than those of $Dy_2Ti_2O_7$ suggest that other factors beyond the chemical pressure effect should play a role in determining the low-temperature magnetic properties of $Dy_2Pt_2O_7$. As in the case of $Gd_2Pt_2O_7$,[13] we attribute the enhanced $|J_{nn}|$ in $Dy_2Pt_2O_7$ to the extra superexchange pathways through the empty e_g orbitals of Pt^{4+} via Dy–O–Pt–O–Dy. This contribution becomes prominent in $Dy_2Pt_2O_7$ having the spatially more extended Pt 5d orbitals.

Table 1. Lattice parameter and selected magnetic parameters for the Dy-pyrochlore spin ices $Dy_2B_2O_7$ (B = Ge, Ti, Pt, Sn).

$Dy_2B_2O_7$	Ge	Ti	Pt	Sn
IR(B^{4+})/Å	0.53	0.605	0.625	0.69
a/Å	9.93	10.10	10.1913(1)	10.40
θ_{CW}/K	0	0.5	0.77	1.7
D_{nn}/K	2.47	2.35	2.29	2.15
C_{peak}/J·(mol-Dy)$^{-1}$·K^{-1}	3.17	2.72	2.80	2.65
T_{peak}/K	0.828	1.25	1.13	1.20
J_{nn}/D_{nn}	−0.73	−0.49	−0.56	−0.46
J_{eff}/K	0.67	1.2	1.01	1.16
Ref.	[11]	[11]	this work	[11]

4. Conclusion

In summary, we have synthesized the cubic pyrochlore $Dy_2Pt_2O_7$ under 4 GPa and 1000 ℃, and confirmed it to be a new classical spin ice as $Dy_2Ti_2O_7$. The magnetic specific heat of $Dy_2Pt_2O_7$ signals a moderate enhancement of $|J_{nn}|$, but the ratio $J_{nn}/D_{nn} = -0.56$ remains located in the spin ice regime as predicted by DSIM. Our work demonstrates that the J_{nn}/D_{nn} can be effectively tuned by replacing the B-site cation of Ising pyrochlores. But further explorations are needed to realize a transition from spin ice to an antiferromagnetically ordered state by varying J_{nn}/D_{nn} in a larger range as predicated by the DSIM.

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