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Chemical pressure effects on pyrochlore spin ice

H. D. Zhou,[1,*] J. G. Cheng,[2] A. M. Hallas,[3] C. R. Wiebe,[1,3,4] G. Li,[1]
L. Balicas,[1] J. S. Zhou,[2] J. B. Goodenough,[2] J. S. Gardner,[5,6] and E. S. Choi[1]

[1]*National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306-4005, USA*
[2]*Texas Materials Institute, University of Texas at Austin, Austin, TX 78712, USA*
[3]*Department of Chemistry, University of Manitoba, Winnipeg, MB R3T 2N2 Canada*
[4]*Department of Chemistry, University of Winnipeg, Winnipeg, MB, R3B 2E9 Canada*
[5]*NIST Center for Neutron Research, Gaithersburg, Maryland, 20899-6102, USA*
[6]*Indiana University, 2401 Milo B. Sampson Lane, Bloomington, Indiana 47408, USA*

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A comparison among the two sets of studied pyrochlore spin ices: $Ho_2Sn_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Ge_2O_7$ with Ho^{3+} spins, and $Dy_2Sn_2O_7$, $Dy_2Ti_2O_7$, and $Dy_2Ge_2O_7$ with Dy^{3+} spins, shows that the application of chemical pressure through each set drives the system toward the antiferromagnetic phase boundary from the spin ice region, which agrees with the prediction of the "dipolar spin ice" model of den Hertog and Gingras. Among all the studied pyrochlore spin ices, $Dy_2Ge_2O_7$ has the smallest ratio of J_{nn}/D_{nn} = -0.73.

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The pyrochlores, denoted by the formula $A_2B_2O_7$, belong to a special class of geometrically frustrated materials that have provided a fascinating and diverse set of low temperature magnetic states, from spin liquid to spin glass through spin ice behavior[1]. Spin ice is a very special case, in which the magnetic rare earth ions (A) are situated on the vertices of a lattice of corner sharing tetrahedra. Due to the local crystalline field, the magnetic ground states of these ions are Ising-like, pointing along the <111> axis that joins the centers of two neighboring tetrahedra. The balance between the dipolar and exchange interactions between spins results in a short-range ordered ground state for each magnetic tetrahedron with two spins pointing in and two pointing out. This has a direct analogy to the two-short, two-long proton bond disorder about each oxygen atom in water ice. In fact, the calculation of the low temperature entropy in spin ice can be mapped onto the water ice problem to yield S = R(ln2-1/2ln(3/2)). This gives a zero point entropy 1/2Rln(3/2), which is same as the entropy Pauling predicted for water ice[2]. In the literatures, four pyrochlores: $Ho_2Ti_2O_7$[3,4], $Ho_2Sn_2O_7$[5–7], $Dy_2Ti_2O_7$[8–11], and $Dy_2Sn_2O_7$[12,13], have been confirmed as spin ices. The search for new spin ices is still an active field of condensed matter physics, made more intriguing by the observation of emergent monopole excitations that has captured the attention of the broader scientific community[14–19].

The low temperature magnetic properties of a pyrochlore spin ice are controlled by the magnetic exchange (J_{nn}) and dipolar interaction (D_{nn}) of the nearest-neighbor spins. The theoretical phase diagram for spin ices, first elucidated by den Hertog and Gingras using the so called "dipolar spin ice" model (DSIM)[20], indicated that there is a critical range of values over which a spin ice is stable: $J_{nn}/D_{nn} > -0.91$. For $J_{nn}/D_{nn} < -0.91$, the system undergoes a transition to a low temperature Q = 0 antiferromagnetically ordered state. To verify this phase diagram, it would be ideal to have the ability to vary J_{nn}/D_{nn} to induce a long-range magnetic ordering from the spin ice state. Until now, there have been very few studies which emphasize this approach. Mirebeau and Goncharenko[21] completed neutron scattering studies with an actual applied pressure of 6.0 GPa on $Ho_2Ti_2O_7$ which should change the J_{nn}/D_{nn} ratio. A long-ranged magnetic ordering phase transition was not observed. An alternative method to efficiently change the J_{nn}/D_{nn} ratio is to apply chemical pressure or change the lattice parameter. For the pyrochlore lattice, the dipolar interaction can be calculated as $D_{nn} = 5/3(\mu_0/4\pi)\mu^2/r^3_{nn}$ (where r_{nn} is the nearest-neighbor rare earth spin distance). Meanwhile, J_{nn} is expected to be more sensitive to changes in the lattice parameter, or the distance between the rare earth spins.

With this approach in mind, we have undertaken a high temperature high pressure method to synthesize germanate pyrochlores which have considerably smaller lattice parameters than the stanates and titanates. Prepared with conventional solid state reactions under ambient pressure, $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$ are pyrogermanates with a tetragonal structure[22]. Although their spin relaxation behaviours are analogous to that of the pyrochlore spin ice, they undergo a transition to a long-ranged magnetic ordering at 1.6 K for $Ho_2Ge_2O_7$[23] and 2.2 K for $Dy_2Ge_2O_7$[24]. Shannon and Sleight reported that the cubic pyrochlore phase prepared under high pressure has a lattice parameter of 9.9 Å[25], which is smaller than other canonical spin ices (typically $a > 10.0$ Å). Recently we have successfully prepared pyrochlore $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$ under 7 GPa and 1000 °C by using a high temperature and high-pressure (HTHP) technique[26]. We also reported both of them to be spin ices[27,28]. In this letter, by comparing two sets of the studied pyrochlore spin ices: $Ho_2Sn_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Ge_2O_7$ with Ho^{3+} spins, and $Dy_2Sn_2O_7$, $Dy_2Ti_2O_7$, and $Dy_2Ge_2O_7$ with Dy^{3+} spins, we found that the application of chemical pressure through each set drives

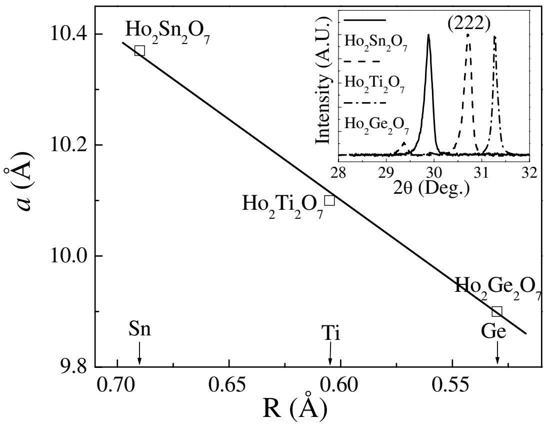

FIG. 1: (a) The variances of the lattice parameter for $Ho_2Sn_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Ge_2O_7$ with the radius of Sn^{4+}, Ti^{4+}, and Ge^{4+} ions. Inset: the (222) peak from XRD patterns for $Ho_2Sn_2O_7$, $Ho_2Ge_2O_7$, and $Ho_2Ti_2O_7$. The line is just a guide for the eye.

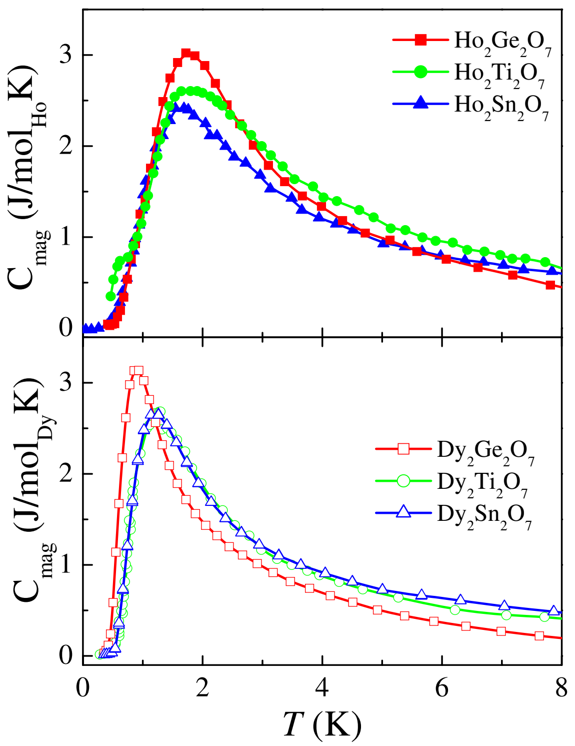

FIG. 2: (Color online) The magnetic specific heat, C_{mag} for all six pyrochlore spin ices. The data for $Ho_2Sn_2O_7$ is from Ref[6], for $Ho_2Ti_2O_7$ is from Ref[4], and for $Dy_2Ti_2O_7$ is from Ref[8].

TABLE I: The lattice parameters and selected magnetic parameters for all six pyrochlore spin ices

	a	θ_{CW}	D_{nn}	C_{peak}	T_{peak}	J_{nn}/D_{nn}	J_{eff}
	Å	K	K	J/mol$_{Ho, Dy}$K	K		K
$Ho_2Sn_2O_7$	10.37	1.8	2.17	2.41	1.65	-0.26	1.61
$Ho_2Ti_2O_7$	10.10	1.9	2.35	2.61	1.75	-0.27	1.72
$Ho_2Ge_2O_7$	9.90	0.06	2.50	3.04	1.70	-0.35	1.63
$Dy_2Sn_2O_7$	10.40	1.7	2.15	2.65	1.20	-0.46	1.16
$Dy_2Ti_2O_7$	10.10	0.5	2.35	2.72	1.25	-0.49	1.20
$Dy_2Ge_2O_7$	9.93	0.0	2.47	3.17	0.828	-0.73	0.67

the system toward the antiferromagnetic (AFM) phase boundary from the spin ice region, which agrees with the prediction of DSIM. $Dy_2Ge_2O_7$ clearly lies on the phase boundary, and put the germanate pyrochlores into context with the rest of the known spin ices with respect to the approach of the first order antiferromagnetic zone boundary and possible quantum critical point.

The lattice parameters of the pyrochlore $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$ prepared by the HTHP method are $a = 9.9026(6)$ Å and $a = 9.9290(5)$ Å, respectively. In order of $Ho_2Sn_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Ge_2O_7$, the (222) peak from the room temperature x-ray diffraction pattern (XRD) shifts tward a higher 2θ (Inset of Fig. 1(a)), implying a decrease in the lattice parameter. Indeed, due to the decreasing radius from Sn^{4+} to Ti^{4+} and to Ge^{4+} ions, the lattice parameter for Ho^{3+}-spin ices decreases respectively (Fig. 1). There is a same trend for the lattice parameters for $Dy_2Sn_2O_7$, $Dy_2Ti_2O_7$, and $Dy_2Ge_2O_7$ samples. With this decrease in the lattice parameter, the chemical pressure imposed by the chemical substitution of the B site ions increases.

In order to study the effect of chemical pressure on two sets of studied pyrochlore spin ices: $Ho_2Sn_2O_7$, $Ho_2Ti_2O_7$, and $Ho_2Ge_2O_7$ with Ho^{3+} spins, and $Dy_2Sn_2O_7$, $Dy_2Ti_2O_7$, and $Dy_2Ge_2O_7$ with Dy^{3+} spins, the specific heat data for all six samples are shown in Fig. 2. Their lattice parameters and selected magnetic parameters are also listed in Table I. The specific heat for the germanates were measured in a Physical Property Measurement System(PPMS) and the measurement uncertainty is around 2%. The magnetic specific heat $C_{mag}(T)$ is obtained by the subtraction of the non-magnetic lattice contribution ($C_P(T)$ of $Lu_2Ti_2O_7$ with no magnetic ions). For $Ho_2Ge_2O_7$, a low temperature nuclear Schottky anomaly of Holmium was also subtracted, following the same method used for $Ho_2Sn_2O_7$[6]and $Ho_2Ti_2O_7$[4], (see supplementary materials for detail)[29]. From $Ho_2Sn_2O_7$ to $Ho_2Ti_2O_7$ (or from $Dy_2Sn_2O_7$ to $Dy_2Ti_2O_7$), the increasing chemical pressure due to the shrinkage of the lattice gives a 8% increase of D_{nn}. The values for both θ_{CW} (Curie temperature) and specific heat peak, C_{peak}, are similar between these two Ho (or Dy) samples. From $Ho_2Sn_2O_7$ to $Ho_2Ge_2O_7$ (or from $Dy_2Sn_2O_7$ to $Dy_2Ge_2O_7$), the increasing chemical pressure gives a 15% increase of D_{nn}. The $\theta_{CW} = 0.06$ K for $Ho_2Ge_2O_7$ or $\theta_{CW} = 0.0$ K for $Dy_2Ge_2O_7$ is much smaller than that of $Ho_2Sn_2O_7$ or $Dy_2Sn_2O_7$. In addition, C_{peak} increases from 2.41 J/mol$_{Ho}$-K for $Ho_2Sn_2O_7$[6] to 3.04 J/mol$_{Ho}$-K for $Ho_2Ge_2O_7$ or from 2.65 J/mol$_{Dy}$-K for $Dy_2Sn_2O_7$ to 3.17 J/mol$_{Dy}$-K for $Dy_2Ge_2O_7$.

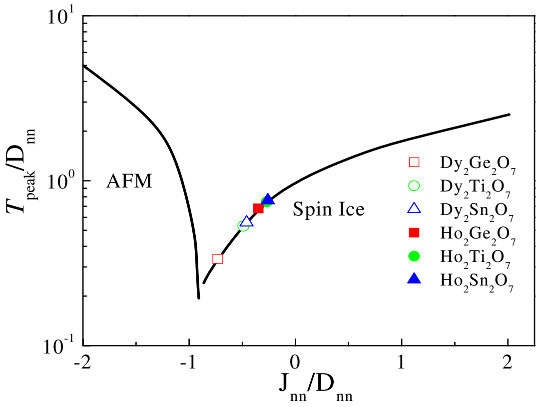

FIG. 3: (Color online) Dependencies of the specific heat peak position $T_{\rm peak}/D_{nn}$ on J_{nn}/D_{nn} ratio. The open symbols are experimental results and the solid lines are the theoretical calculations from "dipolar spin ice" model, Ref[20]

For a pyrochlore spin ice, as DSIM proposed, $\theta_{\rm CW}$ should be on the same energy scale as the effective exchange interaction $J_{eff} = J_{nn} + D_{nn}$ due to the comparable energy scale between J_{nn} and D_{nn}. With similar D_{nn}, the smaller $\theta_{\rm CW}$ indicates a more negative value of J_{nn}, and a more negative value for J_{nn}/D_{nn}. In order to extract the J_{nn}/D_{nn} values for all six samples, we compared the experimental values of $T_{\rm peak}$ to the theoretical calculation of $T_{\rm peak}/D_{nn} \sim J_{nn}/D_{nn}$ curve (Fig. 3) from DSIM. The analysis gives a J_{nn}/D_{nn} = -0.35 for $Ho_2Ge_2O_7$ which is more negative than -0.22 and -0.14 for $Ho_2Ti_2O_7$ and $Ho_2Sn_2O_7$, respectively. The same trend is also found for Dy^{3+}-spin ices: J_{nn}/D_{nn} = -0.73 for $Dy_2Ge_2O_7$ which is more negative than -0.49 and -0.46 for $Dy_2Ti_2O_7$ and $Dy_2Sn_2O_7$, respectively. These values of J_{nn}/D_{nn} are consistent with the experimental results that $\theta_{\rm CW}$ is smaller for $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$. The analysis also shows that the pyrochlore spin ices are driven toward the antiferromagnetic phase boundary with the increasing chemical pressure, as shown in Fig. 3. The DSIM predicted that as the spin ice/antiferromagnetism phase boundary is approached from the spin ice side, the specific heat peak becomes narrower and the peak height begins to increase in magnitude[30], which are also consistent with the experimental specific data. The sharp increase of J_{nn}/D_{nn} = -0.73 for $Dy_2Ge_2O_7$ actually reflects the sharp increase of $C_{\rm peak}$ calculated from DSIM as the spin ice system approaches $J_{nn}/D_{nn} < -0.5$[30]. With the J_{nn}/D_{nn} obtained here, the calculated $J_{\rm eff}$ for $Dy_2Ti_2O_7$ and $Dy_2Ge_2O_7$ are 1.20 K and 0.67 K respectively. These values are close to the values obtained by fitting the specific heat with a Debye-Hückel theory[27], which are 1.1 K for $Dy_2Ti_2O_7$ and 0.62 K for $Dy_2Ge_2O_7$.

For pyrochlore spin ices, J_{nn} is more sensitive to the application of chemical pressure than that of D_{nn}. Calcultaed for the J_{nn}/D_{nn} ratio, the absolute value of J_{nn} increases 55% (or 82%) from $Ho_2Sn_2O_7$ to $Ho_2Ge_2O_7$ (or from $Dy_2Sn_2O_7$ to $Dy_2Ge_2O_7$), which is larger than the increase of D_{nn}, 15%, between them. Obviously, the effect of chemical pressure on the spin ice state is not linear. The increasing chemical pressure does not result in a large difference between $Ho_2Sn_2O_7$($Dy_2Sn_2O_7$) and $Ho_2Ti_2O_7$($Dy_2Ti_2O_7$), but increases J_{nn}/D_{nn} ratio dramatically between $Ho_2Sn_2O_7$($Dy_2Sn_2O_7$) and $Ho_2Ge_2O_7$($Dy_2Ge_2O_7$). We can compare the effect of chemical pressure to that of physically applied pressure across the series of pyrochlores. We cannot find structure studies under pressure for Ho and Dy pyrochlores, but studies of XRD under pressure for $Tb_2Ti_2O_7$ show that 25 GPa pressure roughly leads to a 10% volume decrease[31]. Changing the lattice from $Ho_2Sn_2O_7$($Dy_2Sn_2O_7$) to $Ho_2Ge_2O_7$($Dy_2Ge_2O_7$), the chemical pressure leads to a 13% volume decrease. This is larger than the effect of 25 GPa pressure on $Tb_2Ti_2O_7$. Under so high chemical pressure, $Ho_2Ge_2O_7$ and $Dy_2Ge_2O_7$ are still spin ices although they move toward the spin ice/antiferromagnetism phase boundary significantly. It is not surprising that 6 GPa pressure on $Ho_2Ti_2O_7$ can not induce a magnetic ordering. The robustness of the pyrochlore spin ice is mainly due to the J_{nn}/D_{nn} ratio, which sufficiently puts the system far away from the phase boundary. As soon as the J_{nn}/D_{nn} ratio approaches the phase boundary, the system should be more sensitive to pressure or chemical pressure. For example, 6 GPa of pressure successfully induces a magnetic ordering from the spin liquid state of pyrochlore $Tb_2Ti_2O_7$[32], in which the estimated $J_{nn}/D_{nn} \sim$ - 1.0, which is in the vicinity of the phase boundary[20]. However, low-lying crystal fields add an addition perturbation to the system which is not considered in the DSIM phase diagram[33].

So far no pyrochlore systems with Ho^{3+} or Dy^{3+} have been found to exhibit the Q = 0 antiferromagnetically ordered state with $J_{nn}/D_{nn} < -0.91$, which was proposed by DSIM. Here we discuss two experimental possibilities to probe this quantum critical point: (i) Following the chemical pressure route to synthesize pyrochlore systems with even smaller lattice parameters than those of germanates. One natural thought is to synthesize pyrochlore $Ho_2Si_2O_7$ or $Dy_2Si_2O_7$ since the radius of Si^{4+} (R = 0.4 Å) ion is smaller than that of Ge^{4+} (R = 0.53 Å) ion. The structural stability limits for pyrochlore phases ($A_2B_2O_7$) can be defined by the ionic radius ratios, $R_{A^{3+}}/R_{B^{4+}}$, which extends in the range of $1.36 < R_{A^{3+}}/R_{B^{4+}} < 1.71$ at ambient pressure for most pyrochlores. This is the reason why germanates prepared under ambient pressure are tetragonal, since $R_{Ho^{3+}}/R_{Ge^{4+}} = 1.92$ and $R_{Dy^{3+}}/R_{Ge^{4+}} = 1.94$. The size mismatch between Ho^{3+}(Dy^{3+}) and Ge^{4+} is too large to stabilize a pyrochlore structure. For silicates with $R_{Ho^{3+}}/R_{Si^{4+}} = 2.54$ and $R_{Dy^{3+}}/R_{Si^{4+}} = 2.57$, even larger size mismatch, under ambient pressure the structure is triclinic $P\bar{1}$. Studies have shown that under 10 GPa and 1600 ∼ 1700 °C, $Dy_2Si_2O_7$ still maintains a triclinic structure although its lattice parameter decreases[34]. Therefore, the synthesis of pyrochlore silicates under extremely high pressure is a challenge for future studies. (ii) Adding pressure on $Dy_2Ge_2O_7$. As we discussed above, when J_{nn}/D_{nn} ratio is close to the phase boundary, the system should be more sensitive to pressure. For $Dy_2Ge_2O_7$, J_{nn}/D_{nn} = - 0.73 is reasonably close to the critical value - 0.91. There is a higher probability for high pressure to induce a magnetic ordering state in $Dy_2Ge_2O_7$, compared to other pyrochlore spin ices. The pressure needed is expected to be higher than 6 GPa, which is the pressure needed to induce magnetic ordering in $Tb_2Ti_2O_7$ with smaller J_{nn}/D_{nn} = - 1.0. Future studies such as low temperature susceptibility and neutron scattering measurements under high pressures are needed.

In summary, increasing the chemical pressure through the pyrochlore spin ice series significantly affects J_{nn}, which drives the system toward the spin ice/antiferromagnetism phase boundary. For $Dy_2Ge_2O_7$, J_{nn}/D_{nn} = -0.73 is the smallest known ratio in the series. Future studies on this new system, will help to elucidate the critical spin behaviour of a spin ice approaching the edge of the phase boundary, and may lead to newly discovered Higgs phases in this limit.[35] Within this regime, the density of monopoles at low temperatures is expected to be high, and new physics involving Bjerrum pairing may become relevant[27].

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[*] Electronic address: `zhou@magnet.fsu.edu`

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