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. Choi1
1National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306-4005, USA
2Texas Materials Institute, University of Texas at Austin, Austin, Texas 78712, USA
3Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada
4Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba R3B 2E9, Canada
5NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6102, USA
6Indiana University, 2401 Milo B. Sampson Lane, Bloomington, Indiana 47408, USA

(Received 16 January 2012; published 18 May 2012)

A comparison among the two sets of studied pyrochlore spin ices, Ho2Sn2O7, Ho2Ti2O7, and Ho2Ge2O7 with Ho3+ spins and Dy2Sn2O7, Dy2Ti2O7, and Dy2Ge2O7 with Dy3+ 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, Dy2Ge2O7 has the smallest ratio of $J_{nn}/D_{nn} = -0.73$.

DOI: 10.1103/PhysRevLett.108.207206 PACS numbers: 75.30.Kz, 75.30.Cr, 75.40.Cx, 75.50.Lk

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 $S = R[\ln 2 - 1/2\ln(3/2)]$. This gives a zero-point entropy $1/2R\ln(3/2)$, which is same as the entropy Pauling predicted for water ice [2]. In the literature, four pyrochlores, Ho2Ti2O7 [3,4], Ho2Sn2O7 [5–7], Dy2Ti2O7 [8–11], and Dy2Sn2O7 [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 have 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 $Q = 0$ anti-ferromagnetically 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 Ho2Ti2O7, 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 $D_{nn} = 5/3(\mu_0/4\pi)\mu^2/r_{nn}^3$ (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, Ho2Ge2O7 and Dy2Ge2O7 are pyrogermanates with a tetragonal structure [22]. Although their spin relaxation behaviors are analogous to that of the pyrochlore spin ice, they undergo a transition to a long-ranged magnetic ordering at 1.6 K for Ho2Ge2O7 [23] and 2.2 K for Dy2Ge2O7 [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 Ho2Ge2O7 and Dy2Ge2O7 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$_2$Sn$_2$O$_7$, Ho$_2$Ti$_2$O$_7$, and Ho$_2$Ge$_2$O$_7$ with Ho$_{3+}$ spin $J$ and Dy$_2$Sn$_2$O$_7$, Dy$_2$Ti$_2$O$_7$, and Dy$_2$Ge$_2$O$_7$ with Dy$_{3+}$ spins, we found that the application of chemical pressure through each set drives the system toward the antiferromagnetic (AFM) phase boundary from the spin ice region, which agrees with the prediction of the DSIM. Dy$_2$Ge$_2$O$_7$ clearly lies on the phase boundary and possible quantum critical point.

The lattice parameters of the pyrochlore Ho$_2$Ge$_2$O$_7$ and Dy$_2$Ge$_2$O$_7$ prepared by the HTHP method are $a = 9.9026(6)$ Å and $a = 9.9290(5)$ Å, respectively. In order of Ho$_2$Sn$_2$O$_7$, Ho$_2$Ti$_2$O$_7$, and Ho$_2$Ge$_2$O$_7$, the (222) peak from the room-temperature x-ray diffraction pattern (XRD) shifts toward a higher $2\theta$ [inset of Fig. 1(a)], implying a decrease in the lattice parameter. Indeed, due to the decreasing radius from Sn$^{4+}$ to Ti$^{4+}$ 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$_2$Sn$_2$O$_7$, Dy$_2$Ti$_2$O$_7$, and Dy$_2$Ge$_2$O$_7$ 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$_2$Sn$_2$O$_7$, Ho$_2$Ti$_2$O$_7$, and Ho$_2$Ge$_2$O$_7$ with Ho$^{3+}$ spin $J$ and Dy$_2$Sn$_2$O$_7$, Dy$_2$Ti$_2$O$_7$, and Dy$_2$Ge$_2$O$_7$ with Dy$^{3+}$ spins, the magnetic 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 heats for the germanates were measured in a physical property measurement system (PPMS), and the measurement uncertainty is around $2\%$. The magnetic specific heat $C_{\text{mag}}(T)$ is obtained by the subtraction of the nonmagnetic lattice contribution [$C_P(T)$ of Lu$_2$Ti$_2$O$_7$ with no magnetic ions]. For Ho$_2$Ge$_2$O$_7$, a low-temperature nuclear Schottky anomaly of holmium was also subtracted, following the same method used for Ho$_2$Sn$_2$O$_7$ [6] and Ho$_2$Ti$_2$O$_7$ [4] (see Supplemental Material for detail [29]). From Ho$_2$Sn$_2$O$_7$ to Ho$_2$Ti$_2$O$_7$ (or from Dy$_2$Sn$_2$O$_7$ to Dy$_2$Ti$_2$O$_7$), the increasing chemical pressure due to the shrinkage of the lattice gives an 8% increase of $D_{nn}$. The values for both $\theta_{\text{CW}}$ (Curie temperature) and specific heat peak $C_{\text{peak}}$ are similar for these two Ho (or Dy) samples. From Ho$_2$Sn$_2$O$_7$ to Ho$_2$Ge$_2$O$_7$ (or from Dy$_2$Sn$_2$O$_7$ to Dy$_2$Ge$_2$O$_7$), the increasing chemical pressure gives a 15% increase of $D_{nn}$. The value of $\theta_{\text{CW}} = 0.06$ K for Ho$_2$Ge$_2$O$_7$ (or $\theta_{\text{CW}} = 0.0$ K for Dy$_2$Ge$_2$O$_7$) is much smaller than that of Ho$_2$Sn$_2$O$_7$ or Dy$_2$Sn$_2$O$_7$. In addition, $C_{\text{peak}}$ increases from 2.41 J/molHo $\cdot$ K for Ho$_2$Sn$_2$O$_7$ [6] to 3.04 J/molHo $\cdot$ K for Ho$_2$Ge$_2$O$_7$ or from 2.65 J/molDy $\cdot$ K for Dy$_2$Sn$_2$O$_7$ to 3.17 J/molDy $\cdot$ K for Dy$_2$Ge$_2$O$_7$.

For a pyrochlore spin ice, as the DSIM proposed, $\theta_{\text{CW}}$ should be on the same energy scale as the effective exchange interaction $J_{\text{eff}} = J_{nn} + D_{nn}$ due to the comparable energy scale between $J_{nn}$ and $D_{nn}$. With similar $D_{nn}$, the smaller $\theta_{\text{CW}}$ value indicates a more negative value of $J_{nn}$ and a more negative value for $J_{nn}/D_{nn}$. To extract the $J_{nn}/D_{nn}$ values for all six samples, we compared the experimental values of $T_{\text{peak}}$ to the theoretical calculation of $T_{\text{peak}}/D_{nn} \sim J_{nn}/D_{nn}$ curve (Fig. 3) from the DSIM. The analysis gives a value of $J_{nn}/D_{nn} = -0.35$ for Ho$_2$Ge$_2$O$_7$, which is more negative than $-0.22$ and

![FIG. 1.](image-url) (a) Variances of the lattice parameter for Ho$_2$Sn$_2$O$_7$, Ho$_2$Ti$_2$O$_7$, and Ho$_2$Ge$_2$O$_7$ with the radius of Sn$^{4+}$, Ti$^{4+}$, and Ge$^{4+}$ ions. Inset: the (222) peak from XRD patterns for Ho$_2$Sn$_2$O$_7$, Ho$_2$Ge$_2$O$_7$, and Ho$_2$Ti$_2$O$_7$. The line is a guide for the eye.

![FIG. 2.](image-url) (color online). Magnetic specific heat, $C_{\text{mag}}$, for all six pyrochlore spin ices. The data for Ho$_2$Sn$_2$O$_7$ are from Ref. [6]; Ho$_2$Ti$_2$O$_7$, from Ref. [4]; and Dy$_2$Ti$_2$O$_7$, from Ref. [8].
also consistent with the experimental specific heat data.

These values of $J_{nn}/D_{nn}$ are close to the values obtained by fitting the specific heat with a Debye-Hückel theory [27], which are 1.20 and 0.67 K, respectively. These values are 1.1 K for Dy$_2$Ti$_2$O$_7$, which is more negative than −0.49 and −0.46 for Dy$_2$Ti$_2$O$_7$ and Dy$_2$Sn$_2$O$_7$, respectively. The sharp increase of $J_{nn}/D_{nn}$ actually reflects the sharp increase of $C_{peak}$ calculated from the DSIM as the spin ice system approaches the spin-ice–antiferromagnetism phase boundary from a Debye-Hückel theory [27], which are 1.1 K for Dy$_2$Ti$_2$O$_7$ and 0.62 K for Dy$_2$Ge$_2$O$_7$.

For pyrochlore spin ices, $J_{nn}$ values are more sensitive to the application of chemical pressure than $D_{nn}$ values. Calculated for the $J_{nn}/D_{nn}$ ratio, the absolute value of $J_{nn}$ increases 55% (or 82%) from Ho$_2$Sn$_2$O$_7$ to Ho$_2$Ge$_2$O$_7$ (or from Dy$_2$Sn$_2$O$_7$ to Dy$_2$Ge$_2$O$_7$), 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$_2$Sn$_2$O$_7$ (Dy$_2$Sn$_2$O$_7$) and Ho$_2$Ti$_2$O$_7$ (Dy$_2$Ti$_2$O$_7$), but increases the $J_{nn}/D_{nn}$ ratio dramatically between Ho$_2$Sn$_2$O$_7$ (Dy$_2$Sn$_2$O$_7$) and Ho$_2$Ge$_2$O$_7$ (Dy$_2$Ge$_2$O$_7$). We can compare the effect of chemical pressure to that of physically applied pressure across the series of pyrochlores. We cannot find structure studies for Ho and Dy pyrochlores under pressure, but XRD studies for Tb$_2$Ti$_2$O$_7$ under pressure show that a 25 GPa pressure roughly leads to a 10% volume decrease [31]. On the changing of the lattice from Ho$_2$Sn$_2$O$_7$ (Dy$_2$Sn$_2$O$_7$) to Ho$_2$Ge$_2$O$_7$ (Dy$_2$Ge$_2$O$_7$), the chemical pressure leads to a 13% volume decrease. This is larger than the effect of a 25 GPa pressure on Tb$_2$Ti$_2$O$_7$.

Under so high chemical pressure, Ho$_2$Ge$_2$O$_7$ and Dy$_2$Ge$_2$O$_7$ 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$_2$Ti$_2$O$_7$ cannot induce a magnetic ordering. The robustness of the pyrochlore spin ice is mainly due to the $J_{nn}/D_{nn}$ ratio, which puts the system sufficiently far 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$_2$Ti$_2$O$_7$ [32], in which the estimated value $J_{nn}/D_{nn} \sim -1.0$, which is in the vicinity of the phase boundary [20]. However, low-lying crystal fields add an additional 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 the 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$_2$Si$_2$O$_7$ or Dy$_2$Si$_2$O$_7$, 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, $R_{A^{4+}}/R_{B^{4+}}$, which extend in the range of 1.36 < $R_{A^{4+}}/R_{B^{4+}}$ < 1.71 at ambient pressure for most pyrochlores. This is the reason that 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 $R_{Dy^{3+}}/R_{Si^{4+}} = 2.57$, an even larger size mismatch, under ambient pressure the structure is triclinic P1. Studies have shown that under 10 GPa and 1600–1700 °C, Dy$_2$Si$_2$O$_7$...
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 Dy2Ge2O7. As we discussed above, when the $J_{nn}/D_{nn}$ ratio is close to the phase boundary, the system should be more sensitive to pressure. For Dy2Ge2O7, $J_{nn}/D_{nn} = -0.73$ is reasonably close to the critical value of $-0.91$. Compared to other pyrochlore spin ices, there is a higher probability for high pressure to induce a magnetic ordering state in Dy2Ge2O7. The pressure needed is expected to be higher than 6 GPa, which is the pressure needed to induce magnetic ordering in Tb2Ti2O7 with a smaller value of $J_{nn}/D_{nn} = -1.0$. 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 Dy2Ge2O7, $J_{nn}/D_{nn} = -0.73$ is the smallest known ratio in the series. Future studies on this new system will help to elucidate the critical spin behavior 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].

This work utilized facilities supported in part by the NSF through the Cooperative Agreement No. DMR-0654118 and the State of Florida. C.R.W. acknowledges support through NSERC, CFI and the ACS Petroleum Fund. J.S.Z. and J.B.G. are grateful for financial support from NSF DMR-0904282 and DMR-1122603 and the Robert A. Welch Foundation (No. F-1066). L.B. is supported by DOE-BES through Grant No. DE-SC0002613.

*zhou@magnet.fsu.edu

[28] A paper about detailed characterizations of Ho2Ge2O7 is to be published.