

## CHCRUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

## Antiferromagnetic order in the pyrochlores $R_{2}Ge_{2}O_{7}$ (R=Er,Yb)

Z. L. Dun, X. Li, R. S. Freitas, E. Arrighi, C. R. Dela Cruz, M. Lee, E. S. Choi, H. B. Cao, H. J. Silverstein, C. R. Wiebe, J. G. Cheng, and H. D. Zhou
Phys. Rev. B 92, 140407 — Published 7 October 2015
DOI: 10.1103/PhysRevB.92.140407

## Antiferromagnetic order in the pyrochlores $R_2Ge_2O_7$ (R = Er, Yb)

Z. L. Dun,<sup>1</sup> X. Li,<sup>2</sup> R. S. Freitas,<sup>3</sup> E. Arrighi,<sup>3</sup> C. R. Dela Cruz,<sup>4</sup> M. Lee,<sup>5,6</sup> E. S. Choi,<sup>6</sup>

H. B. Cao,<sup>4</sup> H. J. Silverstein,<sup>7</sup> C. R. Wiebe,<sup>6,7,8,9</sup> J. G. Cheng,<sup>2</sup> and H. D. Zhou<sup>1,6</sup>

<sup>1</sup>Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200, USA

<sup>2</sup>Beijing National Laboratory for Condensed Matter Physics,

and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

<sup>3</sup>Instituto de Fisica, Universidade de Sao Paulo, CP 66318, 05314-970, Sao Paulo, SP, Brazil

<sup>4</sup>Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37381, USA

<sup>5</sup>Department of Physics, Florida State University, Tallahassee, FL 32306-3016, USA

<sup>6</sup>National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310-3706, USA

<sup>7</sup>Department of Chemistry, University of Manitoba, Winnipeg, MB R3T 2N2 Canada

<sup>8</sup>Department of Chemistry, University of Winnipeg, Winnipeg, MB, R3B 2E9 Canada

<sup>9</sup>Canadian Institute for Advanced Research, Toronto, Ontario, M5G 1Z7, Canada

(Dated: September 22, 2015)

Elastic neutron scattering, ac susceptibility, and specific heat experiments on the pyrochlores  $Er_2Ge_2O_7$  and  $Yb_2Ge_2O_7$  show that both systems are antiferromagnetically ordered in the  $\Gamma_5$  manifold. The ground state is a  $\psi_3$  phase for the Er sample and a  $\psi_2$  or  $\psi_3$  phase for the Yb sample, which suggests "Order by Disorder" (ObD) physics. Furthermore, we unify the various magnetic ground states of all known  $R_2X_2O_7$  (R = Er, Yb, X = Sn, Ti, Ge) compounds through the enlarged XY type exchange interaction  $J_{\pm}$  under chemical pressure. The mechanism for this evolution is discussed in terms of the phase diagram proposed in the theoretical study [Wong et al., Phys. Rev. B 88, 144402, (2013)].

PACS numbers: 75.10.Jm, 61.05.fm, 75.40.-s

The pyrochlores  $R_2X_2O_7$  (R: rare earth elements, X : transition metals) have been a hot topic due to their emergent physical properties based on the geometrically frustrated lattice<sup>1,2</sup>. Recent interest in pyrochlores is focused on systems with effective spin-1/2 R<sup>3+</sup> ions<sup>3,4</sup>, in which the crystal electric field (CEF) normally introduces a well-isolated Kramers doublet ground state with easy XY planar anisotropy<sup>5,6</sup>. In these XY pyrochlores, the anisotropic nearest neighbor exchange interaction  $J_{ex} = (J_{zz}, J_{\pm}, J_{z\pm}, J_{\pm\pm})$  between the R<sup>3+</sup> ions, plus the strong quantum spin fluctuations of the effective spin-1/2 moment, stabilize various exotic magnetic ground states<sup>3</sup>.

 $Er_2Ti_2O_7$  and  $Yb_2Ti_2O_7$  are two celebrated examples of the effective spin-1/2 XY pyrochlores. For Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, the local [111] Ising-like exchange interaction  $J_{zz}$  is considerably larger than the XY planar interaction  $J_{\pm}^{7}$ . An unconventional first order transition is observed<sup>8</sup>, which has been proposed to be a splayed-ferromagnet (SF) state with  $Yb^{3+}$  spins pointing along one of the global major axes with a canting angle<sup>9</sup>. For  $Er_2Ti_2O_7$ , the  $Er^{3+}$  spins are energetically favored to lie within the local XY plane due to the dominating  $J_+$ , in which an accidental U(1) degeneracy is preserved in the Hamiltonian at the mean-field level that allows the  $\mathrm{Er}^{3+}$  spins to rotate continu-ously in the XY plane<sup>10-13</sup>. Recently, both experimental and theoretical studies suggest that the quantum spin fluctuations lift the U(1) degeneracy with a small gap opening in the spin-wave spectrum and select an antiferromagnetic (AFM) ordering state  $(\psi_2)$  as the ground state for Er<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. This is the so called "order by disorder" (ObD) mechanism $^{13-17}$ , in which the ground state is selected through entropic effects. Meanwhile, an alternative CEF-induced energetic selection mechanism is proposed that will likewise result in the  $\psi_2$  state with similar value of the gap<sup>18,19</sup>.

These delicate magnetic ground states are fragile and easily affected by perturbations, such as chemical pressure. By replacing the Ti<sup>4+</sup> sites with the nonmagnetic  $\operatorname{Sn}^{4+}$  and  $\operatorname{Ge}^{4+}$  ions, the lattice parameter varies to changes the exchange interactions. As listed in Table I, for both  $Er_2X_2O_7$  and  $Yb_2X_2O_7$  series, the Curie temperature and ordering temperature increase with decreasing lattice parameter. Moreover, their magnetic ground states are markedly different.  $Er_2Sn_2O_7$  does not show any long-range magnetic ordering down to 50  $mK^{20}$  but displays a spin freezing below 200 mK with the AFM Palmer-Chalker (PC) correlations<sup>21</sup>. It is proposed that  $Er_2Sn_2O_7$  is approaching the  $\psi_2/PC$  phase boundary where the selection of either state is weak  $^{21-23}$ .  $Er_2Ge_2O_7$  shows an AFM ordering<sup>24</sup> that is similar to  $Er_2Ti_2O_7$ . While a similar SF phase is observed for both  $Yb_2Ti_2O_7$  and  $Yb_2Sn_2O_7^{25-27}$ ,  $Yb_2Ge_2O_7$  strikingly displays AFM ordering at  $T_N = 0.61 \text{ K}^{28}$ . So far, the exact nature of the magnetic ground states of Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> are not clear. Are they also selected by ObD mechanism<sup>29</sup>? More importantly, while the theoretical studies  $^{3,22,23}$  have made significant efforts to unify the magnetic properties of Yb and Er-XY pyrochlores, unified magnetic phase diagrams have not been experimentally achieved.

In this manuscript, we studied the polycrystalline pyrochlores  $Er_2Ge_2O_7$  and  $Yb_2Ge_2O_7$  using elastic neutron scattering under magnetic fields, ac susceptibility, and

TABLE I: Comparison between Er<sub>2</sub>X<sub>2</sub>O<sub>7</sub> and Yb<sub>2</sub>X<sub>2</sub>O<sub>7</sub>.

	$Er_2X_2O_7$			$Yb_2X_2O_7$		
X site ion	Sn	Ti	Ge	Sn	Ti	Ge
$IR(X^{4+})(Å)$	0.69	0.605	0.53	0.69	0.605	0.53
$a(\text{\AA})$	10.35	10.07	9.88	10.28	10.03	9.83
$\theta_{CW}(\mathbf{K})$	-14	-15.9	-21.9	0.53	0.75	0.9
$T_N$	$\sim$	1.17	1.41	0.15	0.24	0.62
Order type	$\sim$ (AFM)	AFM	AFM	FM	$\mathbf{FM}$	AFM
Reference	21	30	24	25	8	28
Spin state	$\sim$ (PC)	$\psi_2$	$\psi_3$	SF	$\mathbf{SF}$	$\psi_{2(or3)}$
Reference	21	14	this work	25	9	this work



FIG. 1: (color online) Elastic neutron scattering patterns and Rietveld refinements for  $\text{Er}_2\text{Ge}_2\text{O}_7$  at (a)T = 3 K and H = 0 T, (b)T = 0.3 K and H = 0 T, and (c)T = 0.3 K and H = 5 T. (d) The field dependence of the (200) and (311) Bragg Peaks intensities measured at T = 0.3 K, the critical field H<sub>c</sub> is marked as the dash line. The spin configurations for (e) $\psi_2$ , (f) $\psi_3$  and (g)splayed-ferromagnetic (SF) phases in the local coordination.

specific heat measurements. We identified a  $\psi_3$  phase for the Er sample and a  $\psi_2$  or  $\psi_3$  phase for the Yb sample (see Fig. 1 (e)(f) for their spin configurations), which suggest ObD mechanism. Furthermore, we unified the various magnetic ground states of all studied R<sub>2</sub>X<sub>2</sub>O<sub>7</sub> (R = Er, Yb, B = Sn, Ti, Ge) through the enlarged XY type exchange interaction  $J_{\pm}$  under chemical pressure. We discussed this general rule in terms of the phase diagram proposed by Wong et al<sup>23</sup>.

Experimental details are listed in the supplemental materials<sup>31</sup>. By comparing the neutron diffraction patterns measured at 3 K and 0.3 K (Fig. 1(a, b)) for

 $Er_2Ge_2O_7$ , several magnetic Bragg peaks, such as (111) (220) (311), etc., are clearly observed at 0.3 K (  $< T_N$ = 1.41 K). The refinements using the XY type AFM spin structure in the  $\Gamma_5$  manifold, either  $\psi_2$  or  $\psi_3$  (Fig. 1(e, f), fit these magnetic Bragg peaks well with a magnetic moment of 3.23(6)  $\mu_B$ . In fact, all magnetic phases within the  $\Gamma_5$  manifold result in the same diffraction pattern and it's impossible to distinguish them in powder samples with zero-field data. Fig .1(d) shows the field dependence of the (220) and (311) Bragg peaks intensities. The details are: (i) with H < 0.15 T, a magnetic domain alignment results in a quick drop of the (220) peak intensity with increasing field; (ii) between 0.15 and 2 T, the spins gradually rotates with the magnetic field but keeps the AFM nature; (iii) around a critical field  $H_c = 2$  T, the (220) Bragg peak intensity abruptly drops to a background value while the (311) Bragg peak intensity continuously increases. This demonstrates that above  $H_c$ ,  $Er_2Ge_2O_7$  enters a spin polarized state. The observed FM (400) and AFM (200) Bragg peaks on the pattern measured at H = 5 T (Fig. 1(c)) suggest that this polarized state is similar to the SF state in the  $\Gamma_9$  manifold. The refinement by assuming one single SF structure with the magnetic field applied along the global z axis (Fig .1(g)) actually fits the powder average 5 T data well with the  $\text{Er}^{3+}$  moment as  $\vec{M} = (\pm 1.42(2), \pm 1.42(2), 4.40(1))$  $\mu_{\rm B}$  in the global coordinate frame. The double peak feature of the reported ac susceptiblity data for Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> also confirmed the magnetic domain alignment around 0.15 T and the critical field around 2 T<sup>24</sup>.

It has been pointed out<sup>14</sup> that (i) for both  $\psi_2$  and  $\psi_3$ states, a multi-domain state with equal fraction of 6 magnetic domains (plotted in the supporting material<sup>31</sup>) at zero field will be expected, which give different intensities of the (220) Bragg peak; (ii) with the applied magnetic field in  $[1\overline{1}0]$  direction, two domains with larger intensity will be selected if the  $\psi_2$  phase is present<sup>10</sup>. This will result in a (220) peak intensity jump, which has been exactly observed for  $Er_2Ti_2O_7$  in the single crystal neutron diffraction experiments<sup>10,13,32</sup>; (iii)similarly, if the  $\psi_3$  state is selected, a decrease is expected for the (220) peak intensity since the two domains with lower intensities will be selected. In our neutron powder diffraction experiment by using a pelleted sample, the magnetic field was applied vertically such that it is perpendicular to the scattering plane. Then a similar selection rule would be expected in addition to a powder averaging effect<sup>31</sup>. As shown in Fig. 1(d), the (220) peak intensity drops dramatically from 400 at 0 T to 250 counts at 0.15 T. This result suggests that  $Er_2Ge_2O_7$  orders in the  $\psi_3$  phase. However, in order to provide unambiguous evidences for the  $\psi_3$  state, polarized neutron experiments on a single crystal sample are needed.

Fig. 2(a) shows the neutron diffraction pattern measured at 0.3 K ( $< T_N = 0.62$  K) for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Due to the small magnetic moment of the Yb<sup>3+</sup> ions, the magnetic Bragg peaks are weak (as shown in the insert). The difference between the 0.3 K and 1.6 K patterns (Fig.



FIG. 2: (color online) (a)Elastic neutron scattering pattern and Rietvelt refinement for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> at T = 0.3 K and H = 0 T. (b) The difference between the patterns measured at 0.3 K (with H = 0 and 2 T) and 1.6 K. (c) The field dependence of the (200), (311) and (400) Bragg Peaks intensities at 0.3 K. (d) The ac susceptibility of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> at different temperatures. Insert: the dc magnetization measured at 0.6 K. (e) The magnetic phase diagram of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>.

2(b)) more clearly shows that the observed magnetic Bragg peaks positions and intensity ratios are very similar to those of  $\text{Er}_2\text{Ge}_2\text{O}_7$ , which identifies  $\text{Yb}_2\text{Ge}_2\text{O}_7$ 's ground state as either  $\psi_2$  or  $\psi_3$  in the  $\Gamma_5$  manifold. Refinements based on these two spin structures give the same  $\text{Yb}^{3+}$  moment of 1.06(7)  $\mu_B$ , which is consistent with the previous report ( $\text{Yb}^{3+} \approx 1.15 \ \mu_B$ )<sup>33</sup>.

With an applied magnetic field on  $Yb_2Ge_2O_7$  (Fig. 2(c), the (220) peak intensity decreases quickly around 0.2 T, which indicates a critical field  $H_c \sim 0.2$  T. Upon  $H_c$ , the (311), (400) magnetic Bragg peaks experience a continuous increase, showing a continuous polarization of Yb<sup>3+</sup> spin towards the direction of the magnetic field. The refinement of the 0.3 K pattern measured under 2 T actually yields a SF state with  $M = (\pm 0.31(5), \pm 0.31(5))$  $(1.57(9))\mu_B$  in the global coordinate frame. The critical field is also confirmed by the ac magnetization measurement (Fig. 2(d)). At 75 mK, the ac susceptibility first shows a peak at 0.12 T due to the domain alignment, and then another peak around  $H_c = 0.22$  T to enter the polarized state. With increasing temperature, both peaks' positions move to lower fields and finally disappear above  $T_N$ . This double peak feature is similar to that of  $Er_2Ge_2O_7^{24}$ . Along with our previous reported ac susceptibility data on  $Yb_2Ge_2O_7^{28}$ , a magnetic phase diagram is plotted in Fig. 2(e). However, due to the weak magnetic signal at (220) and the small  $H_c$ , it's dif-



FIG. 3: (color online) The electronic magnetic specific heat  $C_m$  for (a)Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> and (b)Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. The red dash lines show linear fits of the arrow-marked regions and the blue solid lines show fits considering the spin-wave gap.

ficult to study how exactly this domain alignment affects the (220) peak intensity, which obstructs us to distinguish between  $\psi_2$  and  $\psi_3$ . One noteworthy feature is that the dc magnetization measured at 0.6 K for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> reaches 1.6  $\mu_B$  at 5 T. This value is consistent with that of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and confirms the similar CEF scheme between the Ge and Ti samples<sup>33</sup>.

The selection of either  $\psi_2$  or  $\psi_3$  phase breaks the continuous U(1) symmetry, which requires a pseudo-Goldstone mode with a spin-wave gap below  $T_N$ . For  $Er_2Ti_2O_7$ , the inelastic neutron scattering has confirmed the existence of this gap ( $\sim 50 \ \mu eV$ )<sup>17</sup>. Meanwhile, the specific heat data can reveal the information of this gap. Fig. 3(a) shows the electronic magnetic specific heat  $(C_m)$  of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub><sup>31</sup>. Below  $T_N$ ,  $C_m$  follows an almost prefect  $T^3$  behavior down to 0.2 K, as the red dash line shows. However, it's obvious that  $C_m$  deviates from this straight  $T^3$  line to a lower value below 0.2 K. Contrasting to a Goldstone mode where the  $C_m$  strictly follows a  $T^3$  law, the gap that exists in the pseudo-Goldstone mode will multiply a component  $I_{\Delta}(T)$  to  $T^3$ , which is temperature dependent only in the temperature region that is comparable to the energy gap  $\Delta$ . The relationship between the  $C_m$  and  $\Delta$  has already been derived in the supporting material of Ref.<sup>13</sup>. Here we rewrite it as:

$$C_m^{\Delta} = \frac{\mathcal{N}_A k_B^4 \pi^2 a^3}{120 \,\overline{v}^3} \left( \frac{15}{16 \,\pi^4} \int_0^\infty dX \, \frac{X^2 \left(X^2 + \delta^2\right)}{\sinh^2 \frac{\sqrt{X^2 + \delta^2}}{2}} \right) T^3$$
  
=  $A I_{\Delta}(T) \, T^3$  (1)

where  $\mathcal{N}_A$  is the Avogadro constant,  $k_B$  is the Boltzmann constant, a is the lattice constant,  $\overline{v}$  is the geometric mean of magnon velocity,  $X = \beta k$  and  $\delta = \beta \Delta$ (dimensionless). The integration  $I_{\Delta}(T)$  can be evaluated numerically with a given  $\Delta$ .  $I_{\Delta}(T)$  approaches a unity at high temperatures but decreases quickly when  $k_B T$  is comparable to  $\Delta$ , which leads the deviation of the  $C_m^{\Delta}$ from the  $T^3$  behavior at low temperatures. The best fit of the measured  $C_m$  to Eq. 1 with the  $\Delta$  and A as two variables (blue line in Fig. 3(a)) yields the  $\Delta = 24 \ \mu \text{eV}$ 



FIG. 4: (color online) Magnetic ground state phase diagrams for (a) $Er_2X_2O_7$  series and (b) $Yb_2X_2O_7$  series adopted from Ref.<sup>23</sup>. The dash areas are for just for the illustration purpose. The trends for the chemical pressure effects are shown as the direction of the arrows.

and  $A = 15.67 \text{ J.K}^{-4} \text{mol}^{-1}$ , which corresponds to  $\overline{v} = 45.8 \text{ m/s}$ .

Similar analysis of the  $C_m$  for  $\text{Er}_2\text{Ge}_2\text{O}_7$  (Fig. 3(b)) yields a spin-wave gap  $\Delta = 45 \ \mu\text{eV}$  with A = 1.85 $\text{J.K}^{-4}\text{mol}^{-1}$ (corresponds to  $\overline{v} = 132 \text{ m/s}$ ). One noticed feature is that at high temperatures,  $C_m$  follows a  $T^{2.72}$ (not strict  $T^3$ ) behavior. This could be due to the error bar introduced by the low temperature nuclear Schottky anomaly subtraction.

With the decreasing lattice parameter or the increasing chemical pressure through the Sn to Ti to Ge samples, the magnetic ground states change accordingly (Table I). Given the fact that in these XY pyrochlores, the  $J_{ex}$ dominate the magnetic properties, the chemical pressure can finely tune the  $J_{ex}$  to lead to various magnetic ground states. This change of  $J_{ex}$  is supported by the systematic changes of the Curie temperature and ordering temperature for XY-pyrochlores listed in Table I. Most strikingly, this is the first time to experimentally confirm an AFM  $\psi_{2 or 3}$  phase in Yb-pyrochlores despite the apparently different dominant exchange interactions between Yb and Er-pyrochlores(Ising-like  $J_{zz}$  for Yb-pyrochlores and the XY-planar  $J_{\pm}$  for Er-pyrochlores). This finding indicates there is general rules to unify the various magnetic ground states of all effective spin-1/2 pyrochlores.

Recent theoretical studies have made significant efforts to unify the magnetic ground states of the XYpyrochlores. Wong et al.<sup>23</sup> have scaled the  $J_{ex}$  by  $J_{\pm}$ as three variables (  $J_{zz}/J_{\pm}, J_{z\pm}/J_{\pm}, J_{\pm\pm}/J_{\pm}$ ) and calculated a two dimensional magnetic phase diagram with the fixed ratio of  $J_{zz}/J_{\pm}$ , which contains continuous phase boundaries among the PC, SF,  $\psi_2$  and  $\psi_3$  phases (the phase boundary between  $\psi_2$  and  $\psi_3$  is determined through ObD). By adopting to the exchange interaction values obtained from the inelastic neutron scattering measurements, they successfully located the two Ti samples  $(J_{zz}/J_{\pm} \approx -0.5, J_{z\pm}/J_{\pm} \approx 0, J_{\pm\pm}/J_{\pm} \approx 1.0$  for  $\mathrm{Er}_{2}\mathrm{Ti}_{2}\mathrm{O}_{7}$  and  $J_{zz}/J_{\pm} \approx 3.0, J_{z\pm}/J_{\pm} \approx -2.7, J_{\pm\pm}/J_{\pm} \approx$ 1.0 for Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) in the  $\psi_2$  and SF phase, respectively. Although we are short of knowledge of the exchange interaction values of other XY-pyrochlores, here we located them in the  $J_{zz}/J_{\pm} = -0.5$  and the  $J_{zz}/J_{\pm} = 3.0$  phase diagrams adopted from Ref.<sup>23</sup>. This is based on three facts: (i) the phase diagram areas and boundaries are similar to each other over a wide range value of  $J_{zz}/J_{\pm}$ ; (ii) the ratio of  $J_{zz}/J_{\pm}$  will not dramatically change for each pyrochlore series due to the similar ion anisotropy; (iii) for both compounds, no additional transition nor anomaly is observed from  $T_N$  to the lowest temperature of 50 mK either from the ac susceptibility or the specific heat measurement. This suggests that the 0.3 K spin structure as seen by neutron reflect the nature of its magnetic ground state (T = 0), which in principle could be different from the state selected near the criticality  $(T \leq T_c)^{12,29}$ . As shown in Fig. 4, with increasing chemical pressure, two general trends are obvious: (i) the ground state moves downwards from PC state in  $Er_2Sn_2O_7$  to  $\psi_2$  in  $Er_2Ti_2O_7$ and then  $\psi_3$  in  $\mathrm{Er}_2\mathrm{Ge}_2\mathrm{O}_7$  for the Er-pyrochlores in the  $J_{zz}/J_{\pm} = -0.5$  phase diagram; (ii) the grounds states move rightwards from the SF state of Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> to the  $\psi_2$  or  $\psi_3$  region of Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> in the  $J_{zz}/J_{\pm} = 3.0$  phase diagram.

These two trends can be successfully unified by the scenario that the increasing chemical pressure enhances  $J_{\pm}$ . For Er-pyrochlores with dominant XY type interactions,  $J_{zz}$  and  $J_{z\pm}$  will take small values. Therefore, the increasing  $J_{\pm}$  will primarily decrease the ratio of  $J_{\pm\pm}/J_{\pm}$ to result in a downwards movement of the ground state. On the other hand, for Yb-pyrochlores with dominant local [111] Ising like interactions,  $J_{\pm}$  and  $J_{\pm\pm}$  will take small values. Therefore, the increasing  $J_{\pm}$  will mainly decrease the ratio of  $J_{z\pm}/J_{\pm}$  to result in a rightwards shift of the ground state to reach the AFM state for Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub>. Although without the values of the exchange interactions for all XY-pyrochlores, we cannot conclude the increase of the  $J_{\pm}$  as the only reason for the change of ground states, the comparison between the reported  $J_{\pm}$  values of  $\text{Er}_2\text{Sn}_2\text{O}_7(J_{\pm} = 1.35 \text{ meV})^{21}$  and  $\text{Er}_2\text{Ti}_2\text{O}_7$  $(J_{\pm} = 6.7 \text{ meV})^{13}$  supports our proposed scenario.

Similar to  $Er_2Ti_2O_7$ , the debate arises over what is the microscopic mechanism that breaks the continuous U(1)symmetry and selected the ordered ground state. The selection of different ground states in  $Er_2Ti_2O_7(\psi_2)$  and  $Er_2Ge_2O_7(\psi_3)$  seems to favor the ObD scenario since the selection comes from the quantum fluctuations, which is delicately tuned by the exchange parameters  $J_{ex}^{13-16}$ (Fig. 4). Future experiments are need to explore the potential quantum fluctuations and the possible selection differences between  $T \leq T_c$  and T = 0, which are predicted theoretically within ObD scenario<sup>12,29</sup>. On the other hand, it still remains a theoretical challenge for the CEF-induced energetic selection scenario to explore the possible existence of different spin states, except for the proposed  $\psi_2$  phase for Er pyrochlores<sup>18,19,21</sup>. Furthermore, it is noticed that the values of magnon mean velocity and the gap in Yb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> ( $\bar{v} = 45.8$  m/s,  $\Delta =$ 24  $\mu eV$ ) are both smaller than that of Er<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> ( $\overline{v} =$  $132 \text{ m/s}, \Delta = 45 \mu \text{eV}$ , which is consistent with the ObD mechanism. A smaller  $\overline{v}$  suggests a softer low lying mode in the spin wave spectrum that will result in a smaller

energy difference of spin-wave spectrum between the  $\psi_2$ and  $\psi_3$  phases<sup>13</sup>, for which a smaller gap is expected.

## Acknowledgments

Z.L.D. and H.D.Z. thank the support of NSF-DMR-1350002. R.S.F. acknowledges support from CNPq (400278/2012-0). X.L and J.G.C. is supported by the NSFC (Grant No.11304371) and the Strategic Priority Research Program (B) of the Chinese Academy of Sci-

- <sup>1</sup> J. S. Gardner, M. J. P. Gingras and J. E. Greedan, Rev. Mod. Phys. 82, 53 (2010).
- <sup>2</sup> L. Balents, Nature **464**, 08917 (2010).
- <sup>3</sup> L. Savary and L. Balents, Phys. Rev. Lett., **108**, 037202 (2012).
- <sup>4</sup> S. Onoda, J. Phys.: Conf. Series bf 320, 012065 (2011).
- <sup>5</sup> J. D. M. Champion and P. C. W. Holdsworth, J. Phys.: Condens. Matter 16, S665 (2004).
- <sup>6</sup> H. B. Cao, A. Gukasov, I. Mirebeau, P. Bonville, C. Decorse, G. Dhalenne, Phys. Rev. Lett., **103**, 056402 (2009).
- <sup>7</sup> K. A. Ross, L. Savary, B. D. Gaulin, and L. Balents, Phys. Rev. X 1, 021002 (2011).
- <sup>8</sup> J. A. Hodges, P. Bonville, A. Forget, A. Yaouanc, P. Dalmas de Reotier, G. Andre, M. Rams, K. Krolas, C. Ritter, P. C. M. Gubbens, C. T. Kaiser, P. J. C. King and C. Baines, Phys. Rev. Lett. 88, 077204 (2002).
- <sup>9</sup> L. J. Chang, S. Onoda, Y. Su, Y. J. Kao, K. D. Tsuei, Y. Yasui, K. Kakurai and M.R. Lees, Nat. Commun. 3, 992 (2012).
- <sup>10</sup> J. D. M. Champion, M. J. Harris, P. C. W. Holdsworth, A. S. Wills, G. Balakrishnan, S. T. Bramwell, E. Cizmar, T. Fennell, J. S. Gardner, J. Lago, D. F. McMorrow, M. Orendac, A. Orendacova, D. McK. Paul, R. I. Smith, M. T. F. Telling and A. Wildes, Phys. Rev. B 68, 020401(2003). Rev. Lett. 101, 147205 (2008).
- <sup>11</sup> J. P. C. Ruff, J. P. Clancy, A. Bourque, M. A. White, M. Ramazanoglu, J. S. Gardner, Y. Qiu, J. R. D. Copley, M. B. Johnson, H. A. Dabkowska and B. D. Gaulin, Phys. Rev. Lett. **101**, 147205 (2008).
- <sup>12</sup> B. Javanparast, A. G. R. Day, Z. Hao, and M. J. P. Gingras, Phys. Rev. B **91**, 174424 (2015).
- <sup>13</sup> L.Savary, K. A. Ross, B. D. Gaulin, J. P. C. Ruff and Leon Balents, Phys. Rev. Lett. **109**, 167201 (2012).
- <sup>14</sup> A. Poole, A. S. Wills and E. E. Lelievre-Berna, J. Phys.: Condens. Matter **19**, 452201 (2007).
- <sup>15</sup> P. A. McClarty, P. Stasiak and M. J. P. Gingras, Phys. Rev. B, 89, 024425 (2014).
- <sup>16</sup> M. E. Zhitomirsky, M. V. Gvozdikova, P. C. W. Holdsworth and R. Moessner, Phys. Rev. Lett. **109**, 077204 (2012).
- <sup>17</sup> K. A. Ross, Y. Qiu, J. R. D. Copley, H. A. Dabkowska and B. D. Gaulin, Phys. Rev. Lett., **112**, 057201 (2014).
- <sup>18</sup> S. Petit, J. Robert, S. Guitteny, P. Bonville, C. Decorse, J. Ollivier, H. Mutka, M. J. P. Gingras and I. Mirebeau, Phys. Rev. B, **90**, 060410(R) (2014).
- <sup>19</sup> P. A. Mcclarty, S. H Curnoe and M. J. P. Gingras, J. Phys.

ences (Grants No. XDB07020100). H.J.S. acknowledges support through NSERC (the Vanier program). C.R.W. acknowledges NSERC, CFI, the CRC program (Tier II) and CIFAR. The work at NHMFL is supported by NSF-DMR-1157490 and the State of Florida and the Department of Energy and by the additional funding from NHMFL User Collaboration Support Grant. The work at ORNL High Flux Isotope Reactor was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

: Conf. Ser. 145, 012032 (2009).

- <sup>20</sup> P. M. Sarte, H. J. Silverstein, B. T. K. Van Wyk, J. S. Gardner, Y. Qiu, H. D. Zhou and C. R. Wiebe, J. Phys.: Condens. Matter **23**, 382201 (2011).
- <sup>21</sup> S. Guitteny, S. Petit, E. Lhotel, J. Robert, P. Bonville, A. Forget, and I. Mirebeau, Phys. Rev. B, 88, 134408 (2013).
- <sup>22</sup> H. Yan, O. Benton, L. D. Jaubert, and N. Shannon, arXiv:1311.3501.
- <sup>23</sup> A. W. C. Wong, Z. Hao, and M. J. P. Gingras, Phys. Rev. B, 88, 144402 (2013).
- <sup>24</sup> X. Li, W. M. Li, K. Matsubayashi, Y. Sato, C. Q. Jin, Y. Uwatoko, T. Kawae, A. M. Hallas, C. R. Wiebe, A. M. Arevalo-Lopez, J. P. Attfield, J. S. Gardner, R. S. Freitas, H. D. Zhou, and J.-G. Cheng, Phys. Rev. B **89**, 064409 (2014).
- <sup>25</sup> A. Yaouanc, P. Dalmas de Reotier, P. Bonville, J. A. Hodges, V. Glazkov, L. Keller, V. Sikolenko, M. Bartkowiak, A. Amato, C. Baines, P. J. C. King, P. C. M. Gubbens, and A. Forget, Phys. Rev. Lett. **110**, 127207 (2013).
- <sup>26</sup> Z. L. Dun, E. S. Choi, H. D. Zhou, A. M. Hallas, H. J. Silverstein, Y. Qiu, J. R. D. Copley, J. S. Gardner, and C. R. Wiebe, Phys. Rev. B 87, 134408 (2013).
- <sup>27</sup> J. Lago, I. Zivkovic, J. O. Piatek, P. Alvarez, D. Huvonen, F. L. Pratt, M. Diaz, T. Rojo, Phys. Rev. B 89, 024421 (2014).
- <sup>28</sup> Z. L. Dun, M. Lee, E. S. Choi, A. M. Hallas, C. R. Wiebe, J. S. Gardner, E. Arrighi, R. S. Freitas, A. M. Arevalo-Lopez, J. P. Attfield, H. D. Zhou and J. G. Cheng, Phys. Rev. B **89**, 064401 (2014).
- <sup>29</sup> L. D. C. Jaubert, O. Benton, J. G. Rau, J. Otimaa, R. R. P. Singh, N. Shannon, and M. J. P. Gingras, arXiv:1505.05499.
- <sup>30</sup> P. D. Reotier, A. Yaouanc, Y. Chapuis, S. H. Curnoe, B. Grenier, E. Ressouche, C. Marin, J. Lago, C. Baines and S. R. Giblin, Phys. Rev. B 86, 104424 (2012).
- <sup>31</sup> See Supplemental Material at [URL will be inserted by publisher] for details of sample synthesis, experimental setups, specific heat subtraction, and magnetic domain alignment analysis.
- <sup>32</sup> H. B. Cao, I. Mirebeau, A. Gukasov, P. Bonville, C. Decorse, Phys. Rev. B, 82, 104431 (2010).
- <sup>33</sup> J. A. Hodges, P. Bonville, A. Forget, M. Rams, K. Krolas, and G. Dhalenne, J. Phys.: Condens. Matter **13**, 9301 (2001).